THE INFLUENCE OF FLUORIDES ON THE MICROCRACKING OF ELECTRODEPOSITED CHROMIUM

by

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SUMMARY

Various fluorides were added to a base chromium plating solution to obtain microcracked chromium electrodeposits. Deposition was done on bright nickel plated mild steel substrates and for most of the experimental work a fresh chromium plating solution was used for each test.

The crack counts were statistically analysed and in the case of Hull Cell results multiple regression procedures found quantitative relationships between crack counts and fluoride concentration together with current density. Covering Power, measured with a Hull Cell, was quantitatively influenced by both fluoride concentration and the alkali metal part of the molecule.

Microcracking only occurred within a relatively narrow range of fluoride concentration and a theory is proposed. Simple compounds such as lithium fluoride did not cause microcracking when plating was done in plastic containers but the same solution electrolysed in a glass container gave a microcracked deposit. Fluorosilicates caused microcracking in either glass or plastic containers. A mechanism is suggested for the formation of reaction products of glass and fluorides, these products being similar to fluorosilicates in that they both cause microcracking. The alkali metal part of the fluoride molecule influences microcracking and quantitative relationships were found between microcracking and various parameters of the alkali metal such as atomic number. Caesium is apparently anomalous having a greater effect on microcracking than the other alkali metals. Although the type of fluoride and the alkali metal part of the fluoride molecule influence microcracking the most important effect was found to be fluoride concentration. Since fluorides break down during electrolysis even if only slowly it is incorrect to call them catalysts and some experimental evidence has been found for the incorporation of fluorine into the electrodeposit.

CONTENTS

UNITS

This work was commenced before the introduction of S.I. units and where necessary the appropriate conversions have been made.

CHAPTER 1

INTRODUCTION

Chromium plating[1] has been a commercial undertaking since 1924 almost simultaneously in the U.S.A. and Germany but it was not until 1928 that chromium plating processes were marketed commercially in the U.K.[2,3,4]. Many advances have been made since then in chromium plating solutions although the solutions are essentially the same being based on chromic acid with the addition of sulphate ions. One of the biggest advances was the use of silicofluoride ions as catalysts in addition to sulphate ions[5,6].

Chromium plating[8] is now applied to many different types of articles and for decorative purposes an initial layer of nickel is electrodeposited followed by a final deposit of bright chromium. The usual thickness of bright chromium deposits is about 0.25 to 0.8 microns and is therefore somewhat porous, the thickness of the underlying bright nickel being about 25 microns[9]. British Standard 1224 1970 gives thicknesses of various types of nickel deposit together with the thickness of final chromium deposit required for four types of service conditions.

Under corrosive conditions the chromium is cathodic to the nickel and some degree of corrosion occurs in the nickel because of imperfections in the thin chromium deposit. The nickel deposit gives protection to the basis metal and is itself protected from surface tarnishing by the bright chromium deposit.

Since microcracked chromium is almost always deposited on a bright nickel substrate only those chromium plating processes relevant to this aspect will be discussed although hard chromium[7] deposition is an important industrial process.

Chromium is normally deposited on a commercial scale from aqueous solutions of chromium trioxide, otherwise chromic anhydride CrO_3, commonly called chromic acid. It cannot be deposited from a bath containing only chromic acid; another chemical or chemicals which act as a catalyst must also be present. Sulphuric acid is generally used as one catalyst[8], others being fluorides, silicofluorides[5,6,52] and related compounds. Ways of modifying chromium plating solutions are limited because the strong oxidising properties of chromic acid precludes the use of organic addition agents. Modification is therefore limited to alterations of chromic acid and sulphuric acid concentrations, temperature, current density including wave form changes. The type and concentration of catalyst or the use of several catalysts offers at the present time the only significant changes possible in the formulating of chromium plating solutions.

To improve the corrosion resistance of the electrodeposited chromium various modified chromium electrodeposits have been developed such as microporous[1] chromium, crack-free[1,8] chromium and microcracked[1,8] chromium.

Microporous chromium results from the incorporation of small inert particles in the underlying nickel coating applied as a thin layer subsequent to bright nickel plating. This thin layer is finally bright chromium plated from a conventional chromium plating solution. In service the micropores behave in the same manner as the cracks in microcracked chromium.

Crack-free chromium is usually deposited from fairly high concentration chromic acid solutions since these favour lower stress with consequently fewer cracks. However, these crack-free deposits which are made thicker than decorative chromium are more likely to crack during assembly or in service if they are flexed leading to a macrocrack formation.

Microcracked chromium is deposited from dilute chromic acid solutions containing mixed sulphate/fluoride catalysts such that at a thickness of approximately 1 micron the deposit is uniformly microcracked, that is the chromium has a continuous and uniform network of cracks. When this microcracked chromium is used as the top layer in a decorative nickel plus chromium coating the nickel can be attacked at many of the cracks instead of at a few isolated points as in the case of macrocracked chromium. Whilst this does not prevent attack of the nickel it does provide a large anode area so that corrosion is spread out over a large area and the nickel coating is not penetrated rapidly.

CHAPTER 2

THEORY OF CHROMIUM ELECTRODEPOSITION, FLUORIDE CATALYSED SOLUTIONS AND SOME PROPERTIES OF THE DEPOSIT

The mechanism of chromium deposition is somewhat complicated; much more so than for most metals. Chromium is present in plating solutions in several valency states and various deposition theories have been proposed taking these valency states into account, such as that put forward by Sargent[10] in 1920. Ryan[11] in 1965 reviewed the more recent theories and much Russian[12,13] work has also been done in the last few years.

Sargent[10] developed a chromic acid solution with a sulphate ion as catalyst. He suggested that deposition of chromium occurred from both the trivalent state and the unreduced chromic acid, deposition occurring via a cathode film of a reduced chromium compound. He suggested that the cathode film was nearly neutral, chromic ions partially reducing to chromous ions, and that chromium deposition occurred from both chromic and chromous ions.

Kasper[14] discussed the reduction of chromic acid to various other chromium compounds via a cathode film. The sulphate reaching the film as a complex where it was regenerated and prevented a basic chromium colloid from coating the cathode and interfering with further reduction. Later[15] he suggested that chromium was deposited directly from the hexavalent state.

Ogburn and Brenner[16] by using radioactive chromium showed that the chromium originally present in the bath in the hexavalent state was electrodeposited and that in the trivalent state was not. This tended to confirm the theory that chromium metal deposited directly from the hexavalent state.

Snavely[17] did not agree with Kasper[14] that the reduction of hexavalent chromium to trivalent chromium by atomic hydrogen was thermodynamically impossible. Also, that incorrect conclusions were drawn from Kasper's[15] experiments which showed that chromium was cathodically reduced directly from the hexavalent to the metallic state. Snavely[17] further stated that bright chromium plate was deposited largely as a chromium hydride which decomposed spontaneously to metallic chromium, the hydrogen gas thus formed occluding in any ruptures or irregularities. Large scale shrinking opened up cracks which were then filled with inclusion material drawn from the cathode film.

Although the proposed mechanisms of reduction varied they all agreed with the formation of a cathode film.

Silverman[18] suggested complex formation because of similarities between chromic acid and sulphuric acid. During electrolysis hydrogen ions H^+ moved to the cathode whilst chromate $CrO_4^{=}$ and sulphate $SO_4^{=}$ ions moved towards the anode. The oxygen being in an active state at the anode combined either with chromate ion or chromic acid to form trivalent chromium. Immediately the trivalent chromium and sulphate ions formed known complexes such as $\left(Cr_2(H_2O)_2(SO_4)_2\right)^{++} \left(SO_4\right)^{=}$.

The cation $\left(Cr_2(H_2O)_2(SO_4)_2\right)^{++}$ immediately migrated to the cathode where it discharged resulting in chromium deposition.

Vagramyan and Usachev[26] formed the hypothesis that certain ions, including sulphate, formed chemical compounds with chromic acid and that these compounds could be reduced at the cathode.

Russian[19] workers confirmed the presence of a cathode film by capacitance measurements both in the presence and absence of sulphuric acid. Using radioactive methods they also showed that the chromium apparently formed with the help of chromium ions from the cathode film.

Oscillographic methods used by Solov'eva and Vagramyan[20] also demonstrated the presence of a cathode film. They further showed that trivalent chromium assisted film formation but only when it was freshly formed by electrolytic reduction. Solutions containing trivalent chromium when allowed to stand slowed down the rate of film formation and the film assisting the reduction of chromate ions to the metal was only formed in the presence of sulphuric acid and trivalent chromium.

Usachev and Vagramyan[21] assumed that the only metallic ions that could be reduced were those entering the film as a constituent part of a complex anion, and this is in agreement with Silverman[18].

Usachev[22] studied the formation of trivalent chromium and suggested that it was formed both inside and underneath the cathode film. The chromic acid was reduced with atomic hydrogen catalysed by sulphuric acid as well as by electrochemical reduction.

Chromium complexes are necessary to explain the various complex cathode films and several workers have shown the existence of such complexes. Gabrielson[23] by means of acation exchange resin in the hydrogen form showed that with increasing amounts of trivalent chromium in chromic acid solutions more chromic acid was retained in the resin layer. He concluded that trivalent chromium formed complex compounds with chromate ions which were retained by a cation exchanger in the hydrogen form and that the complexes formed were likely to be positively charged. He[23] suggested that hexavalent chromium was transported to the cathode as positively charged chromium chromate complexes and in a similar way the sulphate ions may be transported to the cathode as positively charged chromium sulphate complexes.

Complex chromium ions containing fluorides have been demonstrated by Scheffer and Hammaker[24] and Chia and King[25]. Scheffer and Hammaker[24] also pointed out that fluoride ions will combine with hydrogen ions giving hydrofluoric acid especially below pH4.

Deposition from fluoride containing electrolytes may thus be explained in a similar[11] way to that for sulphate containing electrolytes.

D. K. Rimdzhiute et al[27] synthesized cathode films from pure chemicals and compared them with those obtained by electrolysis of chromic acid solutions containing sulphate. They showed that electrolytically formed films were analogous in composition to synthetic films, the ratio of Cr^{6+} to Cr^{3+} varying from 1 : 1.7 to 1 : 4.0 being dependent on current density and chromic acid concentration.

Solov'eva et al[28] made extensive studies of the reactions $Cr^{6+} \longrightarrow Cr$, $Cr^{6+} \longrightarrow Cr^{3+}$ and $2H^{+} \longrightarrow H_2$ by measuring the proportion of current corresponding to each of the reactions for different solution compositions. They suggested that when the solution composition is altered changes in the rates of the various reactions occurring at the cathode are due to changes in the composition and properties of the cathode film from which the Cr^{6+} ions are discharged directly.

Jones and Saidington[29] by a microscopic method involving observation of hydrogen evolution and crack formation directly viewed the deposition of chromium from various chromic acid, sulphate solutions onto active and inactive substrates. They found deposition occurred in two stages, an initial one forming a fully coherent deposit and a later stage when the deposit thickened and cracked if the conditions were appropriate. The cracking was cyclic with healing occurring and a new set of cracks occurring at regular time intervals being accompanied by vigorous hydrogen evolution which slowly subsided until the next cycle. Gas evolution occurred almost exclusively from the cracks suggesting that it was due to a low hydrogen overvoltage within the cracks and ceased as a result of bridging by the chromium deposit. Their observations are consistent with the view that the sulphate catalyst controls the nature and extent of the cathode film such that diffusion of some ions to the electrode surface is hindered whilst the penetration of hydrogen ions is still permitted.

Similar work to that of Solov'eva et al[28] was done by Griffin[30] who plated onto nickel substrates from various chromic acid, sulphuric acid solutions at differing current densities, temperatures, chromic acid and sulphuric acid concentrations. By measuring the weight of chromium deposited, the volumes of hydrogen evolved from both the chromium plating solutions and a sulphuric acid eudiometer the chromium metal current efficiency was measured under various plating conditions. The results were produced as two dimensional projections of three dimensional surfaces. The variation of current efficiency in chromium deposition was plotted vertically and related to any two of the four variables temperature, current density, sulphate ratio and chromic acid concentration. For each diagram the data was taken with fixed values of the two remaining variables. This method of presentation illustrated the results very well but it is suggested that multiple regression analysis of these results as well would have allowed all the plating variables to be brought together in a single mathematical model.

Griffin[30] showed that the current efficiency of chromium deposition could be improved by working at high current density and low temperature and that increasing chromic acid concentration tended to reduce the efficiency. The temperature and chromic acid concentration effects were similar to those obtained by Solov'eva et al[28]. Griffin[30] also found other optimum conditions for the electrochemical reduction of Cr^{6+} to chromium metal and of Cr^{6+} to Cr^{3+} and the electrochemical production of hydrogen.

Griffin[30] further determined the effect of the catalytic activity of 23 anions. He concluded from more extensive experiments on 6 anions including fluoride and silicofluoride that there was little or no promise for more efficient catalysts in chromium electrodeposition. His results for fluoride and silicofluoride are not borne out since many commercial chromium plating solutions contain fluorides. The differences in results may be accounted for by the reasonably tight control needed on the variables in order to obtain a satisfactory bright chromium deposit.

A review of mainly Russian literature by Vagramyan and Solov'eva[31] of the theory of chromium deposition was published in 1966, English translation 1969. Their comprehensive review states that the deposition of chromium from chromic acid baths involved the cathodic discharge of a complex multivalent ion whose reduction may lead to the formation of compounds of intermediate valency. During the cathodic deposition of chromium several reactions occur simultaneously and chromate ions can only be reduced in the presence of foreign anions such as sulphate and fluoride.

The cathode film favours the reduction of chromic acid to the metal in contradiction to the existing idea that the film interferes with the free access of chromate ions to the electrode thus hindering the reduction of chromic acid. Oxide layers on the chromium surface act as a great obstacle to the reduction of chromate ions even when the cathode is highly polarised. This shows that the state of the cathode surface is more important than the influence of cathodic polarisation during the reduction of chromate ions.

Because of the small quantities of sulphate present, complexes (presumably sulphate complexes) are probably not formed, it being more probable that sulphate affects the state of the cathode layer thus influencing the electrode process. The action of foreign anions has not been clarified in detail but the rate of partial reduction is dependent on their concentration, in general an increase in concentration favouring production of trivalent chromium. It is possible that sulphate helps to remove trivalent chromium from the cathode surface as well as being adsorbed in preference to oxygen at the cathode.

The structure and composition of the cathode layer was studied by electron microscopy and X-ray diffraction. During electrolysis in the presence of sulphate the film was found to have an appreciable thickness and could be observed visually, its properties changing with the nature of the foreign anions. Film analysis showed that it contained hexavalent chromium, trivalent chromium and sulphate with trivalent chromium and sulphate more concentrated than in the bulk solution, hexavalent chromium being lower.

The current efficiency with respect to the formation of trivalent chromium dropped from sulphate through chloride to fluoride, the inhibition of the hexavalent to trivalent reaction creating favourable conditions for the hexavalent to metallic chromium electroreduction. In general the current efficiency of chromium deposition increased with increase in current density as also shown by Griffin[30].

Temperature increase and stirring should favour removal of reaction products and dissolution of the cathode film, therefore the current efficiency of chromium deposition should decrease under these conditions.

Deposition rate was a function of foreign anion concentration there being a sharp maximum in current efficiency for sulphate but less pronounced for chloride and fluoride probably because of different adsorption and complex formation properties. Foreign anions accelerate the formation of soluble trivalent chromium compounds by complex formation so destroying the film, but they can also assist film formation giving an increase in current efficiency thus leading to a maximum anion effect. The properties and composition of the cathode film are very dependent on the conditions of electrolysis which determines the rate of formation and removal of trivalent chromium from the cathode surface.

This review[31] ended with a discussion of the work of Solov'eva et al[28] and the step-wise reduction of chromic acid[16,17].

Because of the complexities of chromium electrodeposition theory a single theory does not seem possible and the above[31] discusses the effects of changing experimental conditions on chromium deposition. The authors suggested that because of the small quantities of foreign anions present complexes containing them are not formed yet later they suggested that anions may form soluble complex trivalent chromium compounds. This difficulty can be resolved if it is meant that complexes containing foreign anions are only present in the cathode layer and not in the bulk of the electrolyte. Complexes containing foreign anions thus limited would need far less concentration of anions than if the complexes were distributed throughout the electrolyte.

Ryan[11] in his review condensed the available information to the following points:

(1) Chromium electrodeposition takes place through products formed in a cathode film and not directly from ions in the electrolyte.

(2) For maximum current (presumably chromium) efficiency the cathode film must preserve a critical thickness and trivalent chromium ion concentration. Temperature, current density and electrolyte composition all affect the composition of the film.

(3) Hexavalent chromium is reduced in the film both electrolytically and by atomic hydrogen resulting in the formation of complex cations. Added anions stimulate film

formation and act as exchange ions in the creation of a chromic-chromate cation.

(4) The final reduction should involve both a trivalent to divalent chromium ion reduction and a divalent ion to metallic chromium discharge coinciding with the observed deposition potential.

(5) The formation of complex cations from hexavalent chromium, even if only transitory, explains the accumulation of evidence suggesting incorrectly the direct reduction of hexavalent chromium to metallic chromium without any intermediate transitions.

Ryan[11] also concluded that the exact manner by which a chromium ion in the cathode layer is reduced to metal is open to speculation.

FLUORIDE CATALYSED CHROMIUM PLATING SOLUTIONS

Parthasardhy[51] extensively reviewed chromium deposition from fluoride, fluoborate and silicofluoride baths. Exact compositions were given including addition agents together with deposit characteristics, although only brief mention was made of microcracked deposits. He concluded that fluoride baths gave:

1. higher cathode efficiency,
2. greater throwing power,
3. wider bright plating range,
4. possibility of bright deposits from cold baths.

Hairsine, Longland and Postins[50] in a mainly advertising article gave information on single layer microcracked chromium the exact nature of the addition agent not being disclosed.

Hughes[32] gave general principles for the correct operation and control of modern decorative chromium plating baths. In recent times catalysts other than sulphate have been used, such as fluoride and sulphate with fluoride, the cathode efficiencies being about 10% to 15%. Solution and operating conditions were obtained by trial and error, a start being made with a solution containing 400g/l chromic acid and a catalyst ratio of 100 : 1, temperature 45°C and a current density of $10A/dm^2$, the conditions being varied as required. Other conditions being constant, too low a catalyst concentration results in no plate as also does too high a concentration. This is one of the few references that stressed the importance of a satisfactory anodic film of lead peroxide and that the electrical supply should be a good three phase current free from ripple.

Included in the control tests was the Hull Cell, a polished brass cathode being plated at 5 amps for three minutes and a polished nickel plated one at 10 amps for two minutes; with a solution in good order a coverage of 90 mm should be obtained.

Postins[33] gave in chronological order the various types of chromium plating systems that are or have been used in Britain. Improvements have been made to conventional solutions by adjustment of the concentrations of chromic acid and sulphuric acid together with alteration of operating conditions. Many other improvements have been made by additions of small quantities of fluorides and other addition agents, the exact chemical composition and concentration not often being given.

Self-regulating solutions were developed to overcome control problems, sulphate, chromic acid and fluoride concentrations being regulated by the addition of various chemicals so maintaining a correct chromic acid/catalyst ratio under normal operating conditions. Additions made were strontium sulphate to control sulphate, potassium dichromate serving the double purpose of controlling silicofluoride and chromic acid.

Crack free solutions were discussed including proprietary fluoride containing ones. Microdiscontinuous systems were treated similarly to the work of Dennis and Such[1] and The Canning Handbook on Electroplating[8]. Postins[33] pointed out that initially microcracked deposits were obtained from two solutions, the first solution giving essentially a crack free deposit and the second one giving a deposit so highly stressed that it induced microcracking in the layer beneath it. Two solutions were necessary because of the poor covering power of the microcracking solution. A single modern solution operates at 100-280 g/l chromic acid with a mixed catalyst.

It is generally necessary to deposit about 1 micron to achieve satisfactory cracking, cathode efficiencies are about 20% and current densities of 15.0-20.0 A/dm^2 are recommended. The first proprietary single microcracking solution was

Chromic acid	150-170 g/l
Sulphate ratio	300 : 1
Temperature	43°C-46°C
Current density	15-19 A/dm^2
Cathode efficiency	20%

In practice in order to obtain 0.8 microns minimum necessary to obtain good microcracking 8-13 minutes plating was necessary. Various other single layer microcracking solutions were discussed the proprietary catalysts not being disclosed.

Postins[33] next discussed microporous chromium giving the various nickel plating solutions used with the exception of the proprietary inert solids. The time of plating in the second nickel bath containing the inert solids has been reduced to about 20 seconds with modern solutions followed by a deposit of about 0.25 to 0.50 micron of crack free chromium giving a pore count of 15,000-30,000 per 10 mm^2. The system gives corrosion protection comparable to that achieved with microcracked chromium its appearance being virtually indistinguishable from conventional chromium.

A new commercial development is the electrodeposition of a thin, very highly stressed extra layer of nickel onto the bright nickel surface. This is then plated in a conventional chromium plating solution to give a minimum deposit of 0.25 micron, the combined stress of the nickel and chromium layers resulting in microcracking of the chromium.

A recent Process Guide[34] on microdiscontinuous chromium plating processes claims that these systems are accepted today as giving the best corrosion resistance of the various types of nickel chromium plating systems yet developed. The various types of microdiscontinuous chromium plating systems are given in a similar manner to that of Postins[33] except that the various commercial organisations concerned are given. Plant requirements are similar to those for regular chromium plating except that temperature control is more important and that baths based on silicofluoride are rather more aggressive. The plant changes necessary for introducing microdiscontinuous plating into an existing nickel chromium plant are given although this is self-evident once the new plating conditions and solutions have been decided.

Reasonable information is given on deciding which particular process to use commercially and it is pointed out that an incentive for changing from a conventional chromium system can be either to gain an improvement in the corrosion resistance or to maintain at least the same corrosion resistance while plating thinner nickel coatings.

Since with either single layer or double layer microcracked solutions crack density increases with chromium thickness in low current density areas there may be difficulties in obtaining both a sufficient metal thickness and a sufficiently high crack count. Corrosion resistance in deep recesses may therefore be significantly lower than over the rest of the surface. With a microcracked system which depends on the underlying nickel or a microporous system which also depends on the nickel substate the pore or crack density of the final chromium deposit depends largely on the throwing power of the nickel solution. The throwing power of nickel solutions is better than that of chromium solutions and difficulties in recesses may thus be less marked.

In all cases conversion of existing systems to microdiscontinuous chromium will raise plating cost but these additional costs will almost certainly be more than compensated for either by reduced nickel thickness or by keeping nickel thickness the same thus improving the corrosion resistance.

About twenty-seven suppliers of commercial processes are listed together with a selected patent list 1961-1969.

Partington[35] reviewed work on early dual microcracked chromium deposits and discussed difficulties in operating solutions containing selenate and fluorides. The remainder of the paper was devoted to the development of a single stage microcracked chromium process with its obvious advantages. Low chromic acid, high total catalyst content and low temperature were found to be favourable factors for microcracking and high plating efficiency, the process having a cathode efficiency of about 19% at 16 A/dm^2 and about 44^oC. Because sulphuric acid concentration had more effect on covering power than fluoride catalysts and the concentration of the latter had more influence on the crack pattern than sulphuric acid a very low sulphate ratio of from 500 : 1 to 250 : 1 was specified. Partington[35] concluded in agreement with Lindsay, Lovell and Hardesty[92] that thickness taken by itself could be misleading. With a given solution and temperature he[35] found that microcracking occurred at the same time irrespective of current density. However the type and density of microcracking are not independent of current density.

The exact composition of the single stage microcracked chromium plating solution was not disclosed.

Chessin and Seyb[58] using a modified 267 ml Hull Cell found that microcracked chromium could be deposited in two modes. The generally recognised one at high current densities and a second one with somewhat different characteristics at low current densities. The second mode appeared as a narrow band near the low current density end of the Hull Cell panel after nine minutes at 10 amps. As plating time was increased this band extended towards the low current density end.

Time of appearance of the second mode was independent of temperature but dependent on chromic acid concentration and kind and concentration of fluoride type catalyst. The time of first appearance was reduced with increase of silicofluoride. The use of mixed catalysts giving better chromium coverage together with reduced time, the most striking reduction in time being found with addition of small quantities of selenate.

The high current density cracking developed via gross cracks and spangles through to microcracking. The low current density cracking developed via pores and discontinuous hair like cracks both types requiring a minimum thickness of deposit to form.

Although increase of catalyst concentration produced low current density cracking more quickly chromium coverage was generally reduced.

Using a current programming technique they reduced the total plating time necessary to produce homogeneous microcracking on contoured surfaces. Plating was begun at the highest usable current density and then reduced either continuously or in increments.

In their experimental work they found it necessary to give the chromium plated panels a post plating treatment in order to show up the microcracking.

CORROSION RESISTANCE OF MICROCRACKED CHROMIUM

Much information is available on the improved corrosion protection that is obtained from utilising microcracked chromium. Silman[48] gave a general review and Regan[49] discussed the improved resistance and the use of copper to replace some of the bright nickel layer.

Davies[36] prepared samples of various combinations of deposits of bright nickel, semi-bright nickel, bright levelling acid copper, conventional bright chromium and microcracked chromium on substrates of steel, zinc and aluminium. The investigation was mainly concerned with establishing whether microcracked chromium could provide improved corrosion resistance on components nickel plated to Grade 1 standards of B.S. 1224, 1965, now outdated.

Evaluation was done by means of the CASS[38] and Corrodkote[38] accelerated corrosion tests, some static exposure tests also being done in the industrial atmosphere of central Birmingham.

Results of these tests showed that much better corrosion resistance could be obtained when microcracked chromium was used in place of conventional chromium. The thickness of the bright nickel deposit would be reduced by about 30% without undue loss in corrosion resistance when overlaid with microcracked chromium. When both duplex nickel and microcracked chromium are used in combination the nickel thickness may be reduced by about 40%.

Davies[37] also studied the effect of a post plating cathodic treatment in a dichromate filming solution. Subsequent corrosion tests showed that the treatment improved the corrosion resistance of conventional bright chromium but not that of microcracked chromium. The unfilmed microcracked chromium being in any case much superior to that of the filmed conventional chromium.

Dennis and Such[39] did extensive work on the corrosion resistance of decorative nickel and chromium electrodeposits. The procedures used included measurements of open circuit potentials of nickel electrodeposited foils in various electrolytes, anode potentials of foils, accelerated corrosion tests, together with static and mobile outdoor exposure tests. In the sulphur dioxide test the bright nickel plus microcracked chromium corroded most severely because the nickel was attacked at all the discontinuities in the chromium resulting in undermining and flaking of the chromium. In other accelerated tests the microcracked chromium behaved more satisfactorily.

The choice of any particular accelerated corrosion test would depend on whether the test is for quality control or research work. It may well be that the more accelerated a corrosion test is made the less realistic it becomes and so it can then only be used as an acceptance test for one coating system on one basis metal. One of their conclusions was that on static outdoor exposure tests thicker chromium coatings whether crack free or microcracked gave better protection than duplex nickel. In general, microcracked chromium was at least as good as, and in some cases better than conventional chromium taking into account the method of corrosion testing used.

The above short account[36,37,39] of the corrosion resistance of microcracked chromium shows that it is a well established commercial process on a par with other commercial chromium plating processes. It is also included in the latest British Standard Specification BS 1224, 1970.

STRESS IN MICROCRACKED DEPOSITS

Dennis[47] showed that the ductility of composite nickel chromium coatings was usually increased when microcracked chromium was used in preference to decorative or crack free chromium. This would be an advantage under conditions of mild deformation. The development of the crack pattern as a function of plating time was also illustrated.

Most electrodeposits on metals are in a state of internal stress and in the majority of cases this is undesirable because on relief of the stress cracking can occur. However, in the case of microcracked chromium such internal stress is required since on relief the desired microcracking in the deposit is produced.

Gabe and West[41] reviewed the fundamental principles and underlying methods of internal stress measurements. They concluded that the Hoar and Arrowsmith null deflection method gives the most accurate results for general use when their formula in its more approximate form is used.

The principle of the Hoar and Arrowsmith instrument is to measure the force required to maintain in position a flat steel strip, fixed at one end, in terms of an opposing electromagnetic force when the strip is plated on one side. This force is calibrated in terms of a weight. Using this method it is possible to derive an instantaneous stress by considering the restoring force increment needed to be applied when the deposit increases in thickness incrementally.

It is also possible to derive mean stress values and these will be discussed later.

Although measurements have been made of the instantaneous stress[42,46] in the surface layer Gabe and West[43] considered that for chromium where cracking intervenes the concept of a single value instantaneous stress is meaningless. The reason being that the true stress value will vary at any particular point in relation to the proximity and orientation of neighbouring cracks and they therefore only reported mean stress values.

Gabe and West[43] measured stress by the Hoar and Arrowsmith method and the following formula was used to convert the restoring force to mean stress.

$$S = \frac{(4m^3)}{btl(3m - 1)} \times \frac{G}{x}$$

where S = mean stress in gms/(10 mm)^2

m = total length of substrate

b = breadth of substrate

t = thickness of substrate

l = actual plated length of substrate

x = deposit thickness

G = restoring force in gms.

Substrate materials were nickel and mild steel, five chromium plating solutions being used at varying temperatures and current densities and the results plotted as mean stress against chromium thickness.

Deposits from fluoride catalysed and Bornhauser solutions had the largest stress values which were tensile. Variations of current density, temperature and substrate material producing different stress values. High temperature and high current density favoured either stress free or compressively stressed deposits whilst stress in deposits on mild steel were about half those of deposits on nickel. Stress values ranged from about 13000 N/mm^2 tensile to 20000 N/mm^2 compressive but in general were in the range 2500 N/mm^2 compressive.

Various theories put forward to account for the origin of the stresses were:

1. Tensile stresses were due to hydride breakdown although hydrogen diffusion may contribute.
2. Compressive stresses were attributed to volume changes occurring in oxide membranes distributed throughout the deposit as a result of incorporation of some of the cathode film.
3. The fact that deposits could support such high stresses was tentatively attributed to the existence of these oxide membranes.

Constructive criticisms were raised by C. Williams[43] to their theories of the origin of the stresses particularly to the existence of oxide membranes and their relationship with crack patterns in the deposit.

Similar work by Cleghorn and West[44] on thin deposits up to 0.5 microns showed that cathode current efficiency during the first few seconds of plating was very similar to that after eighty seconds. This removed previous criticisms on possible inaccuracies during the first few second of plating because of differencies in cathode current efficiencies. However all the substrate was not immediately covered with chromium. They[44] further showed that the initial compressive stresses could be explained in terms of a single mechanism involving hydrogen diffusion. Some crystallographic evidence for epitaxy was also presented.

In the author's opinion since initial stresses can be caused experimentally by hydrogen the mechanism for the stresses developed in the first few seconds of plating in any chromium plating solution will be the same, because of the low cathode efficiencies giving an intial charge of hydrogen to the substrate surface. Later hydrogen movement is slowed because of a build-up of chromium as suggested by Cleghorn and West[44].

Further work by Cleghorn and West[45] on thin chromium deposits from two plating baths on various substrates suggested possible mechanisms for the initial stresses in deposits and the rapid change from compressive to tensile in the initial stages of deposition. They[45] suggested that coalescence of the initially deposited microcrystallites would give rise to a contraction and hence a tensile stress in the deposit. At the same time the supply of hydrogen to the substrate would be cut off by the now continuous chromium deposit.

The removal of a supply of hydrogen to the substrate combined with crystallite coalescence would tend to produce a rapid compressive to tensile transition in the deposit stress in the thickness range of up to 0.1 microns chromium.

Such and Partington[46] related cracking and internal stress in microcracked chromium deposits. The solution used contained 150 g/1 chromic acid and an unspecified fluoride type catalyst. Plating was done at 22 A/dm^2 for fifteen minutes at 45°C, sulphuric acid contents and trivalent chromium contents were varied as required and substrate materials were steel and bright nickel plated steel.

The Hoar and Arrowsmith method for stress was used and the mean stress was calculated as by Gabe and West[43]. Such and Partington also calculated the instantaneous stress by the following formula:

$$S' = \frac{(4m^3)}{btl(3m - 1)} \times \frac{dG}{dx}$$

where S' = instantaneous stress in a layer of thickness dx deposited when the total thickness was x; in this case dx was the thickness of chromium deposited during thirty second intervals.

dG = corresponding increase in restoring force.

m = total length of substrate.

b = breadth of substrate

t = thickness of substrate.

l = actual plated length of substrate.

Gabe and West[43] concluded that instantaneous stress measurements were meaningless but in the case of microcracked deposits other workers[42,46] found such measurements very useful. Mean stress versus thickness curves for steel substrate from solutions containing varying quantities of sulphuric acid showed that as sulphuric acid concentration increased points of inflexion of the curves moved to lower chromium thicknesses. This was shown much more clearly in the instantaneous stress graphs. No effect of trivalent chromium was observed until above 3 g/l Cr^{+++}.

Crack densities obtained from deposits on rigid steel cathodes increased slowly with thickness but at a certain point, depending on solution composition, suddenly increased from about 160 to about 400 cracks/10 mm during the plating of about 0.7 microns. Increase in crack density after this was less rapid.

Sulphuric acid concentration, all other factors kept constant, was also found to affect the crack density and obviously plays an important role.

With a bright nickel substrate marked differences were found in the stress in the early stages up to a thickness of about 1 micron. The stresses being initially compressive on bright nickel and tensile on steel and after 1 micron the curves were very similar whatever the substrate.

From a study of the instantaneous stress curves which indicated sharp changes very clearly it was found that the crack density increased just as suddenly as the instantaneous stress decreased. Such curves could obviously be used to predict at what thickness microcracking should occur.

A very important conclusion was that stress initiated microcracking, high tensile stresses being relieved by occurrence of microcracking resulting in a bright almost stress free deposit.

Dennis[42] working on the effect of the underlying metal on internal stress in microcracked chromium used the Hoar and Arrowsmith method. Methods of calculation of mean stress and instantaneous stress being the same as those used by Such and Partington[46]. Solution composition was 150 g/l chromic acid 0.35 g/l sulphuric acid and an unspecified fluoride type catalyst. Plating conditions were 15 A/dm^2 for ten minutes at 46°C using fresh solutions daily to avoid trivalent chromium build-up. He showed that some cracks in the same deposit were more clearly defined than others and that the less easily observed ones were in the process of healing over as also suggested by Jones and Saidington[29]. Similar crack patterns were obtained for each of three different bright nickel solutions with no cracking occurring on unpolished dull Watts nickel and unpolished semi-bright nickel. Crack patterns obtained on polished semi-bright nickel, polished steel, polished rolled-nickel, polished sulphamate nickel and polished dull Watts nickel were all similar.

Dennis[42] also found that directional crack patterns occurred when chromium deposition was on polished dull acid, bright acid and cyanide copper deposits, no directionability being found on unpolished bright copper. In general microcracking did not readily occur on matt surfaces while zoned microcracking predominated on bright unpolished surfaces.

The stress versus thickness curves for the chromium were almost identical when chromium was plated onto a substrate with either a tensile or compressive stress. The initial compressive stresses in the chromium could not therefore be due to compressive stresses in the undercoat.

Compressive stresses could be induced by charging substrate materials with electrolytic hydrogen and these induced stresses were of the same magnitude as the compressive regions of the stress curves for chromium. The chromium stress values are therefore the resultants of the true stress in the chromium and the stress induced in the surface layer of the undercoat through hydrogen absorption. As the chromium thickness increases the rate of hydrogen diffusion to the undercoat will be reduced and the rate of hydrogen diffusion away from it may exceed the diffusion rate to it. In this case the compressive stress component caused by hydrogen should become less as the chromium thickness increases. A similar mechanism for initial compressive stresses in microcracked chromium has been proposed by Cleghorn and West[44].

The most important conclusions of Dennis[42] are that surface texture of the undercoat or substrate has the greatest influence on the cracking of elctrodeposited chromium and that instantaneous stress curves show the thickness at which cracking occurs with consequent relief of stress.

ORIGINS OF RESIDUAL STRESS IN ELECTRODEPOSITS

Kushner[53] critically evaluated and reviewed the theories of residual stress in electrodeposited metals together with experimental techniques, mainly for nickel. He gave details of the effects of many variables on stress such as cathode film, temperature, current density, effects of metal surface and addition agents.

His suggested theory for the causes of residual stress was on two basic mechanisms:

1. Lattice misfit in the early layers of the deposit accounting for high internal stress.
2. Water in the aquo complex may remain attached to the metal atom at certain sites in the cathode structure and/or the behaviour of either trapped residues or complex cations in the deposit.

Cleghorn and West[44] together with Dennis[42] suggested that hydrogen could cause initial compressive stresses in chromium alternative mechanisms taking over later. This is in agreement with Kushner[53] in that hydrogen could not be the main cause of residual stress.

RESUME OF FLUORIDE CATALYSED CHROMIUM PLATING SOLUTIONS

Considerable information is available on the methods of production of chromium electrodeposits. The exact nature and composition of addition agents is not always given although much is covered by patents.

Fluorides and related compounds have been used as addition agents for many years, not necessarily to induce microcracking. Hood[52] reported the suggested use of fluorides and fluorosilicates in 1905 and Parthasardhy[51] in 1967 quoted the use of hydrofluoric acid, sodium fluoride, potassium fluoride, ammonium fluoride, sodium fluorosilicate, potassium fluorosilicate and hydrofluosilicic acid. Steiger[54] also reported the use of ammonium fluoride in a cold chromium plating solution. The use of fluoride catalysed baths also produces black chromium deposits[55].

Work on microcracked chromium is reported in the literature in detail except that very little information on the addition agents being used is given other than that the solution contains a suitable quantity of fluoride type catalyst[46] or similar statement.

It appears that no systematic work has been reported on the use of named fluorides and related compounds as addition agents neither has their mode of action received much attention.

Work on stresses in microcracked chromium leads fairly conclusively to the view that microcracking results from the relief of internal stress in the chromium electrodeposit.

CHAPTER 3

EXPERIMENTAL TECHNIQUES

Bright rolled 0.6 mm thick mild steel was used as substrate material, no prior mechanical treatment being necessary before plating. Prior to chromium plating the steel was nickel plated in Cannings Nisol[8] Bright Nickel plating solution.

Steel panels 75 mm x 53 mm were guillotined and a 3.8 mm diameter hole drilled centrally 13 mm from a 53 mm side. Cathodes for the Hull Cell tests were guillotined into 100 mm x 90 mm rectangles and a 3.8 mm diameter hole drilled as near as possible to the edge and at the centre of a 100 mm side.

During preparation it was essential not to touch the surfaces in order to avoid finger marking. To minimise surface deterioration only sufficient steel was cut to last about one week and then individually wrapped in tissue paper. The bulk of the steel was stored in a clean atmosphere covered with its original oil layer.

To keep the anode/cathode geometry constant a perspex cell was used during plating although it was not found necessary to jig the Hull Cell cathodes during nickel plating. The cell was made in 6 mm thick perspex in the form of an oblong box open at both ends and of internal dimensions 50 mm x 75 mm x 150 mm deep. The nickel anode of dimensions 53 mm x 200 mm x 5 mm thick was fixed in slots down one of the 50 mm sides of the box. The bottom of the anode rested on a small perspex platform and the top of the anode projected 50 mm above the box. The cathode was placed directly opposite the anode and was also fixed in slots. The cathode was held in position by means of a brass nut and bolt, the bolt projecting 12 mm from the hole in the cathode into a slot cut through the perspex down the centre of the 53 mm side from the top to a distance of 70 mm. The top of the cathode was then

50 mm below the top of the jig and the bottom of the cathode 25 mm from the bottom of the jig. In addition arrangements were made to air agitate the plating solution by means of a horizontal 9 mm diameter perspex tube pierced with small holes and fitted directly below and parallel to the cathode.

The jig used during chromium plating was similar except that it had no agitation tube and two slots were cut through the perspex near the cathode, one slot in each of the 75 mm x 150 mm sides. The slots 20 mm wide and 100 mm long were cut between 25 mm from the bottom and 50 mm from the top at the edge of the side near the cathode. When in use the jigs were suspended in the plating solution by side arms from the top leaving 25 mm of the jig projecting from the solution.

Cathode electrical connections were made via the brass nut and bolt, the first 150 mm being 1 mm diameter bare copper wire, the final connection to the electrical supply being via smaller diameter insulated copper wire. The two wires were joined by simply twisting and this arrangement led to easy transfer of the cathode when required by simply untwisting.

Electrical connections to both the nickel and lead anodes were made via brass terminals fitted into the anodes well above solution level. In order to avoid poor electrical contacts it was essential to strip down and clean the lead anode connections daily and replace the copper wires weekly. Cleaning of the nickel anode connections was done as required which was about weekly.

Current supply for the nickel plating was rectified single phase A.C. and for the chromium plating rectified three phase A.C.

SOLUTIONS USED DURING PLATING

In all cases soft towns water was used.

1. Anodax[8] Metal Cleaner. This proprietary caustic cleaner was used at 100 g/l, 80°C. The work was made anodic for 1 minute at

6 volts using a mild steel cathode.

2. Klenewell[8] Metal Cleaner. This proprietary cleaner was used at 75 g/l, room temperature to remove any residual surface "dirt" not removed by the Anodax metal cleaner. The work was made cathodic for 1 minute at 5 volts using a mild steel anode.
3. 10% hydrochloric acid, made from 10% by volume chemically pure hydrochloric acid and 90% by volume water, used at room temperature.
4. Nisol[8] Bright Nickel Plating Solution which was made to the following specifications:

Composition		Operating conditions
Nickel Sulphate	300 g	pH 3.6 to 4.2
Sodium chloride	28 g	Temperature 50 to 60°C
Boric acid	40 g	Current density 5 A/dm^2
Water	to 1 litre	Vigorous air agitation

Three litres of solution were made up by dissolving the salts in about 2.5 litres of hot water, filtering and making up to 3 litres and the pH adjusted to 4.0 by carefully adding 10% sodium hydroxide solution, the pH being measured with a Canning[8] Comparator Paper No. 2430 B.

Metallic impurities were removed by electrolysing at a low current density of about 0.2 A/dm^2 at 50°C for about 12 hours using a large mild steel cathode which had been previously nickel plated in the same solution at about 2 A/dm^2 for a few minutes. During low current density electrolysis the solution was continuously and vigorously air agitated. After purification the volume was adjusted to 3 litres and the pH to within the range 3.6 to 4.2 by either 10% hydrochloric acid or 10% sodium hydroxide as necessary. Finally, the Initial Brightener Concentrate for Nisol[8] was added at the rate of 10 mls/litre.

During use the pH rose:was adjusted at least daily by carefully adding 10% hydrochloric acid. Brightening and levelling properties of the solution were maintained by adding Nisol[8] Liquid Brightener at the rate of 0.3 mls/1 amp hour, i.e. 1 ml brightener for every 3 of 75 mm x 50 mm cathodes or 1 ml brightener for every two Hull Cell cathodes.

In order to keep the cell conditions constant the nickel anode was not bagged and for this reason it was necessary to filter the nickel solution every other day. After each plating cycle the nickel anode was mechanically cleaned with a domestic scrubbing brush and water to remove loose surface debris. The nickel solution was replaced every three months because of brightener deterioration.

During nickel plating the solution was vigorously air agitated in addition to the air agitation incorporated into the perspex jig, the nickel plating solution being used in a tall three litre pyrex beaker maintained at 55°C in a thermostatically controlled water bath and evaporation losses made good as necessary.

The following plating procedure was used for nickel plating:

1. Mild steel cathode wired up being careful to only handle the edges.
2. Surface debris removed with cotton wool and acetone.
3. Cleaned anodically in Anodax[8] at 80°C for one minute.
4. Swilled in cold running water.
5. Dipped in cold 10% hydrochloric acid for five seconds.
6. Swilled in cold running water.
7. Cleaned cathodically in Klenewell[8] at room temperature for one minute.
8. Swilled in cold running water.
9. Dipped in cold 10% hydrochloric acid for five seconds.

10. Swilled in cold running water.

11. Plated in Nisol bright nickel plating solution in the jig for thirty minutes at 2 amps, with vigorous air agitation.

12. Swilled in cold running water and immediately transferred to the chromium plating solution.

When nickel plating Hull Cell cathodes no jig was used and a current of 5 amps was used for thirty minutes with vigorous air agitation. During all nickel plating only one side of the cathode was calculated for surface area, deposition occurring mainly on the face directly opposite the anode.

CHROMIUM PLATING

In order to standardise the work one base chromium plating solution[42] was used and this was:

150 g/l	chromic acid
0.35 g/l	sulphuric acid

Plating conditions: 15 A/dm^2 for ten minutes at 46°C.

Fluoride type catalysts were added to the base chromium plating solution and will be discussed later.

In practice a current of 7 amps was used on a 75 mm x 50 mm effective cathode area giving 18.7 amp/dm^2 which would be reduced because of chromium being deposited on the connecting wire and a very small amount round the back of the cathode.

No determinations of chromic acid were made since no chromium plating solution was used for more than a few hours and a large proportion of them were used for only about one hour. However, in view of the low concentration of sulphuric acid the amount present as an impurity in the chromic acid was determined and allowed for when making up the chromium plating solutions.

The anode was of commercially pure lead sheet 2 mm thick which was abraded before each plating sequence with very coarse emery paper and any remaining emery particles removed by rubbing with cotton wool in running water. This constant abrasion reduced the life of a lead anode to about four weeks after which time it became too thin to handle.

The container in which three litres of chromium plating solution was used was either a three litre tall Pyrex beaker or a five litre squat polythene beaker. The solution was maintained at 46°C in a thermostatically controlled water bath under an air extraction hood, evaporation losses being made good as necessary.

FLUORIDE TYPE CATALYSTS

Initially simple fluorides of the alkali metal group were used, namely lithium fluoride, sodium fluoride, potassium fluoride, rubidium fluoride, caesium fluoride and ammonium fluoride.

During the course of the work more complex fluorides containing silicon were used which were lithium fluorosilicate, sodium fluorosilicate, potassium fluorosilicate, caesium fluorosilicate, ammonium fluorosilicate and hydrofluosilicic acid.

Becasue of delays and other problems in obtaining very pure fluorides it was not possible to obtain them all in a very pure state and the following grades were used:

Lithium fluoride, LiF. General purpose reagent.

Sulphate ($SO_4^=$) 0.02% max., Silica (SiO_2) 0.02% max., Iron (Fe) 0.04% max., 98% LiF min.

Sodium fluoride NaF Analar 98% NaF min.

Potassium fluoride KF. Laboratory Reagent, Anhydrous.

Chloride (Cl) 0.02% max., Iron (Fe) 0.02% max., Sodium (Na) 0.5% max., Sulphate ($SO_4^=$) 0.3% max., 97% KF min.

Rubidium fluoride RbF. No impurities quoted.

Caesium fluoride CsF. General Purpose Reagent.

No impurities quoted.

Ammonium fluoride NH_4F. General Purpose Reagent.

Chloride (Cl) 0.01% max., Sulphate ($SO_4^{=}$) 0.02% max., Silica (SiO_2) 0.4% max., Heavy metals and Iron (Fe) 0.05% max., Non volatile matter 0.05% max.

Considerable difficulties were experienced with the supply of rubidium fluoride which when added to chromium plating solutions gave no chromium deposit but only black staining. After several unsuccessful attempts to deposit chormium with this chemical in different chromium plating solutions it was qualitatively analysed[60].

It contained large quantities of nitrates the presence of which was confirmed by the supplier who replaced it. In view of the expense of rubidium fluoride, about £2.00 per gm, it was not possible to do as many tests as would have been desirable.

The following grades of complex fluorides were used:

Lithium fluorosilicate Li_2SiF_6. Not commercially available, made in the laboratory.

Sodium fluorosilicate Na_2SiF_6. Technical quality.

Potassium fluorosilicate K_2SiF_6. Technical quality.

Caesium fluorosilicate Cs_2SiF_6. Not commercially available. Made in the laboratory.

Ammonium fluorosilicate $(NH_4)_2SiF_6$. General purpose reagent.

Hydrofluosilicic acid H_2SiF_6. General purpose reagent, about 30% w/w H_2SiF_6 pure. Wt. per ml about 1.3 gm.

Rubidium fluorosilicate Rb_2SiF_6 was not obtainable commercially and it was not made in the laboratory because of the expense of rubidium salts.

PREPARATION OF LITHIUM FLUOROSILICATE AND CAESIUM FLUOROSILICATE

It was decided to use preparative methods[61] that were simple and did not run the risk of introducing heavy metals such as copper. The method decided on was to react hydrofluosilicic acid with the appropriate carbonate.

$$H_2SiF_6 + Li_2CO_3 \rightarrow Li_2SiF_6 + H_2O + CO_2$$

$$H_2SiF_6 + Cs_2CO_3 \rightarrow Cs_2SiF_6 + H_2O + CO_2$$

The following grades of carbonates were used:

Li_2CO_3	General Purpose Reagent
$Cs_2CO_3 \cdot 2H_2O$	General Purpose Reagent

An alternative method of preparation would be to react hydrofluosilicic acid with the appropriate hydroxide.

$$H_2SiF_6 + 2LiOH \rightarrow Li_2SiF_6 + 2H_2O$$

$$H_2SiF_6 + 2CsOH \rightarrow Cs_2SiF_6 + 2H_2O$$

However, because of the expense of caesium hydroxide, this method of preparation was not used.

The method of preparation used was to weigh the appropriate amount of carbonate into a polythene beaker, dissolve the caesium carbonate in warm water, mix the lithium carbonate to a slurry with warm water, then add with vigorous agitation the appropriate amount of hydrofluosilicic acid.

Completion of reaction was judged to have occurred after fifteen minutes at room temperature when there was no more gas evolution on vigorous agitation. The prepared chemical was immediately added to the chromium plating solution, care being taken to wash out of the container any remaining solution.

ADDITION OF FLUORIDES TO THE CHROMIUM PLATING SOLUTIONS

In order to keep plating condition constant the fluorides were added immediately prior to plating. The appropriate amount of simple fluoride was weighted dissolved in water and added to the chromium plating solution with agitation. In the case of sparingly soluble fluorides they were made into a slurry with warm water and then added.

The same procedure was used for the complex fluorides except that plastic beakers were used and chromium plating was done in a plastic beaker. All possible sources of contamination by silicates were thus removed, the exceptions being the sulphuric acid and some of the solid fluorides supplied in glass containers.

The following plating procedure was used for chromium plating:

1. Chromium plating solution made up but no fluorides added.
2. Volume made up to about 2½ litres and brought up to temperature.
3. Fluoride catalyst added, volume brought up to three litres and temperature adjusted to 46°C.
4. Perspex cell put in with cleaned lead anode.
5. An unplated steel cathode put in the cell immediately after cleaning the steel as in procedures 1 to 10 under bright nickel plating.
6. Current turned on and immediately brought up to 7 amps.
7. After plating for forty minutes current turned off and cathode removed.
8. The cathode was immediately replaced with a freshly bright nickel plated one.
9. Current turned on and plated for ten minutes at 7 amps.
10. Current turned off, cathode removed and swilled in hot water.
11. Thoroughly swilled in cold running water.

12. Dipped in acetone and dried in a current of warm air then nut and bolt removed, care being taken not to handle except at the edges. Labelled on back and stored in a paper envelope in a clean dry atmosphere.

HULL CELL TESTS

The extensively used Hull Cell[62] has attracted much attention being a miniature plating vat having a particular trapezoidal plan and made in various sizes, the most popular being the 267 ml capacity. Sedusky and Mohler[56] discussed its use with various plating solutions but not chromium. Rousselot[57] used a bent cathode because of difficulties in measuring the position where chromium deposition began. Chessin and Seyb[58] used a 267 ml Hull Cell modified by holes in it and immersed in ten litres of chromium plating solution thus giving minimum temperature variations.

Using such a cell it is possible to assess the deposit characteristics at varying current densities all one one cathode.

The 267 mls size was used made in perspex and the following plating procedure adopted:

1. Hull Cell filled with water at 46°C and kept in the thermostatically controlled bath at 46°C.
2. Immediately after chromium plating the 75 mm x 50 mm cathode, the water in the Hull Cell was replaced with 267 mls of this chromium plating solution, measurement being made by a mark on the side of the Hull Cell.
3. A 75 mm x 50 mm mild steel cathode cleaned as previously was chromium plated at five amps for forty minutes using a freshly cleaned Hull Cell lead anode in the remainder of the chromium plating solution left in the beaker. During this time a mild steel Hull Cell cathode was bright nickel plated for thirty minutes.

4. The filmed lead anode was transferred without swilling to the Hull Cell and the nickel plated Hull Cell cathode put in with the current off immediately after removal from the bright nickel solution and swilling.
5. The current was turned on adjusted to 5 amps and plating continued for ten minutes.
6. The current was turned off, the cathode removed and swilled in hot water.
7. Thoroughly swilled in cold running water.
8. Dipped in acetone and dried in a current of warm air, then nut and bolt removed care being taken not to handle except at the edges. Labelled on back and stored in a paper envelope in a clean dry atmosphere.

The lead anode was cut to exactly fit the Hull Cell with the exception that it projected about 25 mm above the top of the cell. This was done for ease of handling and to obtain good electrical connections, in all other respects such as cleaning it was treated as previously. during plating the anode and cathode were kept in position using small "bulldog" clips.

During plating the temperature of the solution in the Hull Cell rose 1°C: this was considered to be insignificant and no attempt was made to keep the temperature constant at 46°C.

In order to find the "best" current for the Hull Cell, plating was done in a chromium plating solution containing 4.844 g/l potassium fluoride which had been previously electrolysed in a glass beaker for forty minutes. Hull Cell cathodes were plated at 2, 3, 4, 5, 6 and 7 amps for ten minutes, using fresh chromium plating solution for each panel.

RESULTS

Amps	No. of Panels Plated	Appearance and Comments
2	1	No deposition, current oscillated
3	1	A little deposition, current oscillated
4	1	More deposition, current oscillated slightly
5	4	More deposition, limited current oscillation
6	2	More deposition, temperature rose to 48°C
7	1	More deposition, temperature rose to 49°C

From the above results 5 amps was chosen.

CRACK COUNTS

These were done using a Vickers optical microscope at a magnification of either x 200 or x 300. The crack pattern was projected onto the screen and counting done in two directions at right angles and the average reading taken. It was not necessary to either treat or etch the surfaces in any way to show up the crack patterns. At the higher crack counts of about 1200 cracks/10 mm it was difficult to be accurate and some degree of estimation was necessary and this was done by rapidly bringing the crack pattern in and out of focus.

To avoid edge effects counting was not done right up to the cathode edges. On the 75 mm x 50 mm cathodes a distance of a few mm was left at either edge before counting across the 50 mm width. This gave the number of readings as either twenty when taking a reading every 2 mm or forty when taking a reading every 1 mm. Due to the distribution of the cracks, it was found convenient to count across the 50 mm width at a distance of 25 mm from the bottom of the cathode, i.e. the bottom being the end remote from the electrical contact end.

Crack counts were also done down the centre of the 75 mm length. In this case readings were taken beginning 1 mm in from the bottom and continuing for a distance of 55 mm. This gave the number of readings as either twenty-eight when taking a reading every 2 mm or fifty-six when taking a reading every 1 mm. In all cases it was not possible to adhere exactly to this number of readings because of location difficulties and in a few cases poor crack patterns.

Location of the positions for counting was done by ruling a wax pencil line vertically down the centre of the cathode and one wax pencil line at right angles to this 25 mm from the bottom of the cathode. Further markers were made on these lines at distances of 18 mm, location between these markers being made using the calibrated stage of the microscope.

Readings taken on the Hull Cell cathodes were located by ruling a wax pencil line 25 mm up from and parallel to the bottom remote from the electrical connection.

The current density at which chromium deposition began on the Hull Cell cathodes was estimated on this line using a ruler with the appropriate non-linear scale. In some cases the thickness of the chromium was so thin where chromium deposition began that a narrow interference fringe about 1 mm wide was formed. In these cases measurements were made from the high current density end to the beginning of the interference fringe.

Measurements of crack counts on Hull Cell cathodes will be discussed later.

REDUCED CHROMIUM

Reduced chromium was introduced either by the natural working of the plating solution or artificially by reduction with oxalic acid $(COOH)_2 \cdot 2H_2O$.

$$2CrO_3 + 3C_2H_2O_4 \rightarrow Cr_2O_3 + 6CO_2 + 2H_2O$$

3.65 g/1 $(COOH)_2\ 2H_2O$ introduced 1 g/1 Cr^{+++}

It was necessary to carefully add the oxalic acid to the chromium plating solutions in order to avoid too vigorous a chemical reaction with consequent loss of solution. This was done by dissolving the requisite amount of oxalic acid in warm water and slowly adding to the plating solution at working temperature over a period of about one hour and then making up to the working volume.

The fluoride catalyst was added immediately after complete addition of the oxalic acid and chromium plating commenced at once.

ANALYSIS OF CHROMIUM PLATING SOLUTIONS AND CHROMIUM DEPOSITS

Trivalent Chromium

Samples of solution were taken for analysis as required and stored in glass containers, care being taken to avoid contact with organic materials such as corks to prevent further reduction. The trivalent chromium was determined spectrophotometrically by the following method[63].

Spectrophotometric Determination of Trivalent Chromium in Chromium Plating Solutions

The method consists of suitably diluting a chromium plating solution and measuring the green colour of the trivalent chromium in the present of a much larger amount of hexavalent chromium. The calibration curve is drawn up using as base solution 450 g/l chromic acid to which is added weighed amounts of oxalic acid to reduce hexavalent chromium to the trivalent form. An addition of 0.73 gm oxalic acid to 100 ml of chromic acid solution gives 2 g/l Cr^{+++}. Suitable standards consist of 2, 4, 6, 8 and 10 g/l Cr^{+++} read at 600 nanometres, dilution x 10 and 5, 10, 15, 20, 25 g/l Cr^{+++} read at the same wavelength, dilution x 25.

For preparation of each standard solution add the required amount of oxalic acid to 100 ml of chromic acid solution, warm gently for ten to fifteen minutes until reduction is complete, cool, dilute to 100 ml with water and then dilute in a standard flask, 5 ml to 50 ml or 2 ml to 50 ml as required.

The calibration curve should be a straight line which will not go through the origin since hexavalent chromium absorbs slightly at this wavelength.

Determination of Sulphate[8,59]

Pipette a 25 ml sample into a 500 ml beaker. Add 50 mls distilled water, 20 mls hydrochloric acid, 50 mls acetic acid and add slowly 20 mls ethanol. Boil until reduced to about one half volume, at least half an hour. Dilute with distilled water to about 400 mls and bring to the boil. Whilst still boiling add dropwise 10 mls 10% barium chloride solution then boil for ten minutes and stand overnight. Filter off the precipitated barium sulphate washing with hot water. Ignite in a platinum crucible, cool in a desiccator and weigh the barium sulphate.

On a 25 ml sample

$$\text{Wt in gms } BaSO_4 \times 16.8 = \text{g/l } H_2SO_4$$

For the determination of sulphuric acid in the chromic acid a 50 gm sample weight was dissolved in water and the above procedure followed.

The amount of sulphuric acid in the chromic acid was found to be 0.056 gms H_2SO_4/100 gms CrO_3 and was taken into account when making up the chromium plating solutions. Sulphuric acid was determined on two chromium plating solutions and found to be 0.34 and 0.36 g/l sulphuric acid, 0.35 g/l being the required figure.

A soluble sulphate can be determined by converting to insoluble barium sulphate by reacting with barium chloride, filtering off and weighing the barium sulphate.

$$H_2SO_4 + BaCl_2 \rightarrow BaSO_4 + 2HCl$$

Interfering elements or compounds which would form an insoluble barium salt must either be removed or converted to a non-reactive form. It is for this reason that the chromium compounds are reduced to the trivalent state by reduction with ethanol.

$$2H_2CrO_4 + 6HCl + 3C_2H_5OH \rightarrow 3\ CH_3CHO + 2CrCl_3 + 8H_2O$$

The hydrochloric acid prevents the hydrolysis of the trivalent chromium and its precipitation as hydroxide. Chromium sulphate formed by the reduction exists in two forms in one of which part of the $SO_4^=$ is attached to the chromium in such a manner as to be unionised and as such would not be precipitated as insoluble barium sulphate. The acetic acid breaks down the covalent or unionised form into the electrovalent form in which form all the $SO_4^=$ can be precipitated as insoluble barium sulphate.

Analysis of the Chromium Deposit

Analysis of the deposit should show up any possible break down products of the fluoride catalysts which may have been co-deposited but because of the small amounts likely to be present physical methods of analysis were best suited. There are chemical methods available for the determination of fluorides[59,64,65] but these were considered to be unreliable[66] for the small amounts probably involved.

The methods used were Electron Probe Microanalysis for the determination of potassium and emission spectroscopy for the determination of rubidium.

Determination of Rubidium

Considerable information is available on emission spectroscopy[67-70] elements have characteristic spectra and for some elements particularly the alkali metals a flame can be used for excitation of the emission spectra[69]. The sample in solution form is atomised and carried as a fine spray into a flame. The chemical elements in the sample are vapourised and stimulated to emit characteristic light rays. This light is deflected into a prism, diffraction grating or selective filter so that only a narrow region of the spectrum characteristic of a particular emitting element is separated and directed onto a suitable detector for measuring light intensity. The detector converts the light into electrical energy which is measured with a recorder. Since such methods are empirical calibration must be done[70].

The alkali metal chosen for analysis was rubidium because the chances of this being an impurity were very remote.

A 75 mm x 50 mm cathode which had been chromium plated from a chromium plating solution in a glass container with 6.667 g/l rubidium fluoride was immersed in a small volume of warm 50% v/v hydrochloric acid until the chromium had been dissolved off the nickel. The specimen was then removed, washed with water and the resultant washings and acid solution evaporated almost to dryness to remove excess hydrochloric acid. The residues were diluted with 5 mls concentrated hydrochloric acid and made up to 100 mls with water in a 100 mls volumetric flask.

An A3000 atomic absorption spectrophotometer loaned by Southern Analytical Ltd. in the emission mode was used for the determination of rubidium in the above prepared solution.

A wavelength of 780 nm was used and with an air/acetylene mixture the flame background was set to zero while spraying distilled water[71]. This was then replaced with the unknown solution and finally with a standard solution containing 5 p.p.m. of rubidium and the results charted by a pen recorder.

Determination of Potassium in Chromium

Detailed[72] and general information[73,74] is available on Electron Probe Microanalysis. The principle of such analysis is simple although in practice the apparatus is complicated and costly. An electron beam is focused to a fine spot at the point on a surface where analysis is required. Impact of the electrons generates X-rays with wavelengths characteristic of the elements present in the illuminated area. These X-rays are sorted by dispersing them with a suitable crystal and their intensities measured, the intensity of each wavelength being proportional to the amount of the corresponding element present in the sample.

The electron beam[73] is generated with an electron gun the beam being controlled by magnetic lens and the whole of the system must be in a vacuum to allow passage of the electron beam. The finely focussed electron beam[73] scans a raster approximately ½ mm square controlled by deflection coils. Part of the scanning beam is reflected while the rest penetrates the surface and is responsible for excitation and X-ray emission. Some of these X-rays pass out of the system via a port and are reflected from the analysing crystal which is rotated to obtain the correct Bragg angle for reflecting the characteristic wavelength of the selected element. These X-rays are then passed to a proportional counter and a trace made on a pen recorder.

For the detection of potassium in the chromium deposit a plating solution was used with the addition of 3.058 g/l potassium fluorosilicate. Plating was done as normal on a 75 mm x 50 mm cathode in a plastic beaker, after bright nickel plating, except that chromium plating time was increased from ten minutes to fifty minutes. Two samples about 50 mm square were cut from the centre of the chromium plated cathode for potassium determination. A trace was also made using potassium chloride as a standard.

Determination of Fluoride in Chromium[91]

The measurement of the γ radiation emitted during the de-excitation of the excited nuclear states provides information about the type and number of nuclei present in the sample without a radioactive nuclide being present as a reaction product. A 500 kilovolt Van de Graff accelerator was used to irradiate the sample with protons and the prompt γ radiation from the $^{19}F(p,\alpha\gamma)^{16}O$ reaction detected.

$$\begin{tikzcd} {}^{19}F + p \arrow[r] & {}^{16}O^{*} + \alpha \arrow[dr] & \\ & & {}^{16}O + \gamma \end{tikzcd}$$

The γ rays were detected using a sodium iodide (thallium) crystal, the integrated yield of the γ rays being proportional to the amount of fluorine present. The absolute amount of fluorine present was estimated by comparing the yield to that of calcium fluoride. The distribution in depth was investigated by varying the proton energy.

A polished copper disc 25 mm diameter x 10 mm thick was electrically connected via a brass screw in the back, degreased, electrochemically cleaned then chromium plated. The plating solution contained 3.0 g/l sodium fluoride and had been prior electrolysed in a glass container for forty minutes with a dummy 75 mm x 50 mm steel cathode at 7 amps. The cleaned copper disc was placed by the side of the dummy cathode and plating continued at 7 amps for a further twenty minutes. All other plating conditions were as previously discussed.

The plated disc was made the target, a vacuum applied and a collimated proton beam of 340 KeV beamed onto the target. The generated rays were detected with a sodium iodide (thallium) crystal coupled to a photomultiplier. The signal from the photomultiplier tube was fed into a 400 channel pulse height analyser via a charged sensitive preamplifier.

The integrated yield was then compared with yield from the standard and the amount of fluorine calculated.

Examination of the electrodeposit at a magnification of x 200 showed that microcracking had occurred.

CHAPTER 4

ANALYTICAL RESULTS AND PHOTOMICROGRAPHS

RUBIDIUM DETERMINATION

Examination of a copy of the trace does not show the presence of rubidium at a level of about 0.5 p.p.m., Fig. 4.1.

FLUORINE DETERMINATION

Sample No.	1	2	3	4
On the surface of the chromium	0.27% F	0.17% F	0.14% F	0.32% F
Inside the chromium	0.011%	0.007% F	0.010% F	0.010% F

POTASSIUM DETERMINATION

No evidence of potassium was found by examination of the trace and an estimation was therefore made by counting the number of disintegrations over a time interval of 100 seconds. The average difference between peak and background of four one hundred second counting times was 1.52 pulses/second.

The corrected number of pulses/second for potassium in potassium chloride was 3360.

$$\%K = \frac{1.52}{3360} \times 100 = 0.045\%$$

The average background count was 50 pulses/second over a 100 second counting period.

$$\text{Standard deviation} = \frac{\sqrt{50}}{\sqrt{100}} = 0.7$$

$$\therefore \text{ 95\% confidence limits} = 0.045 \pm \frac{2 \times 0.7}{3360} \times 100$$

$$= 0.045\% \pm 0.042\%$$

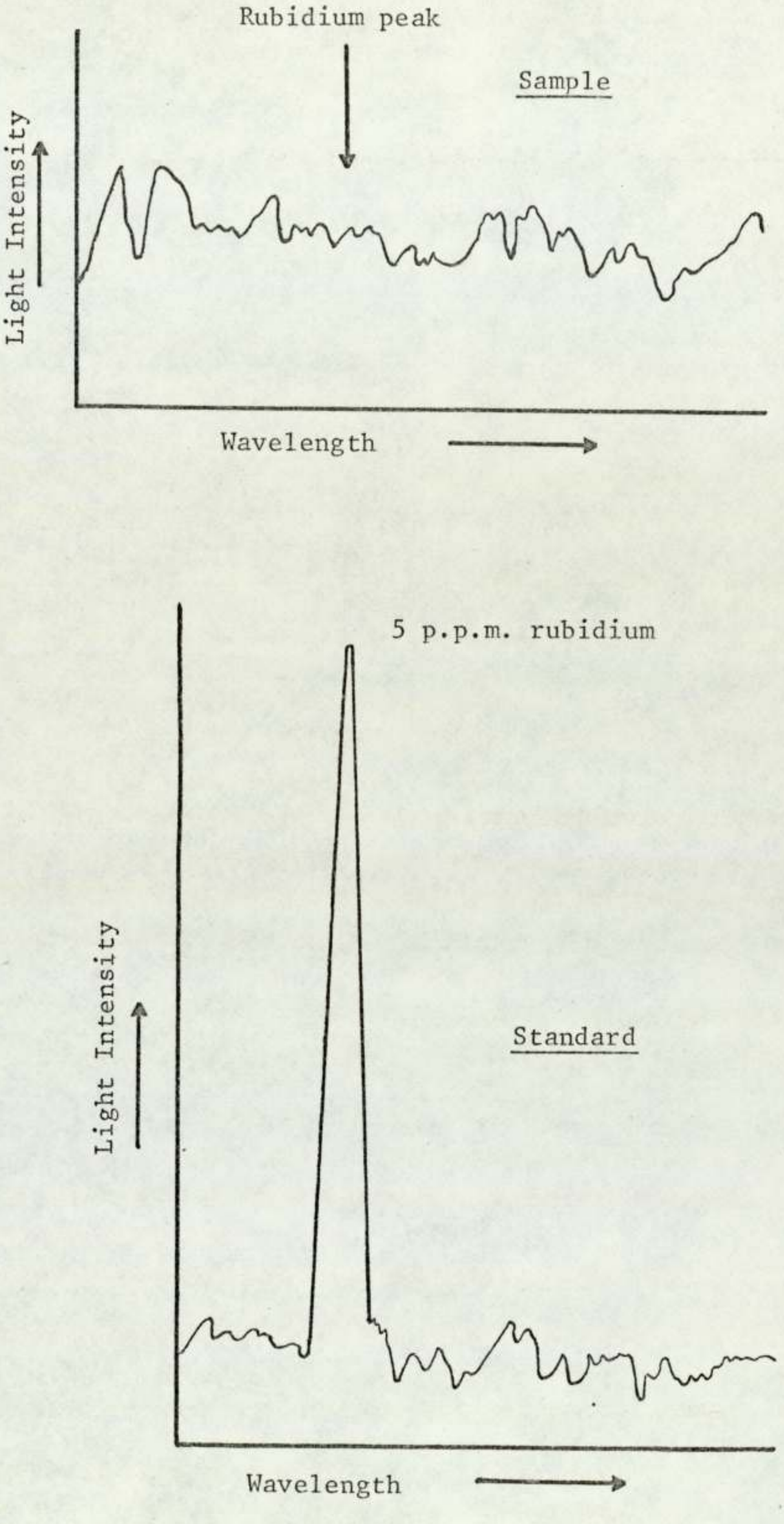

FIG. 4.1. Determination of Rubidium in Microcracked Chromium

$$\%K = 0.045\% \pm 0.042\%$$

This method is not considered sufficiently accurate for the determination of potassium in chromium, the level of potassium, if present, being less than about 0.04%.

PHOTOMICROGRAPHS

The following photomicrographs, all at a magnification of x 200, illustrate the various types of microcracking found. No post plating treatment was necessary and all the photographs were taken on fixed current density cathodes.

Fig. 4.2	4.844 g/l potassium fluoride (1.584 g/l fluoride). This is typical of the crack patterns found at the mid fluoride concentrations. (Taken at the centre of a horizontal line 25 mm from the cathode bottom.)
Fig. 4.3	2.472 g/l ammonium fluorosilicate (1.580 g/l fluoride). This shows the smaller crack density obtained when using an ammonium compound, at an equivalent fluoride concentration, in place of an alkali metal compound. (Taken at the centre of a horizontal line 25 mm from the cathode bottom.)
Fig. 4.4	5.647 g/l caesium fluoride (0.706 g/l fluoride). This shows the commencement of microcracking at a low fluoride concentration. (Taken at the centre of a horizontal line 25 mm from the cathode bottom.)
Fig. 4.5	1.0 g/l hydrofluosilicic acid (0.790 g/l fluoride). This shows the beginning of filling in of the original zoned areas. (Taken at the bottom of the cathode.)
Fig. 4.6	3.528 g/l ammonium fluoride (1.810 g/l fluoride). This shows further filling in of the original zoned areas. (Taken at the centre of a horizontal line 25 mm from the cathode bottom.)

Fig. 4.7 8.813 g/l caesium fluoride (1.102 g/l fluoride). This is similar to Fig. 4.6 some zones have completely filled in, others have not yet begun to fill in. (Taken at the bottom of the cathode.)

Fig. 4.8 5.216 g/l sodium fluorosilicate (3.160 g/l fluoride). This shows the difficulties of counting the cracks at the higher fluoride concentrations, a reasonable estimation could be made by bringing the crack pattern rapidly in and out of focus. (Taken at the centre of a horizontal line 25 mm from the cathode bottom.)

It can be seen that crack counting presented no problems except at the higher fluoride concentrations. All cracks were counted, for example in Fig. 4.2, some cracks are more distinct than others but for counting purposes they were all included.

Recent scanning electron microscope studies by Dennis and Fuggle[93] showed that only certain discontinuities in a microcracked or microporous chromium coating functioned as effective corrosion sites. All the visible microcracks would not then act as anodic sites.

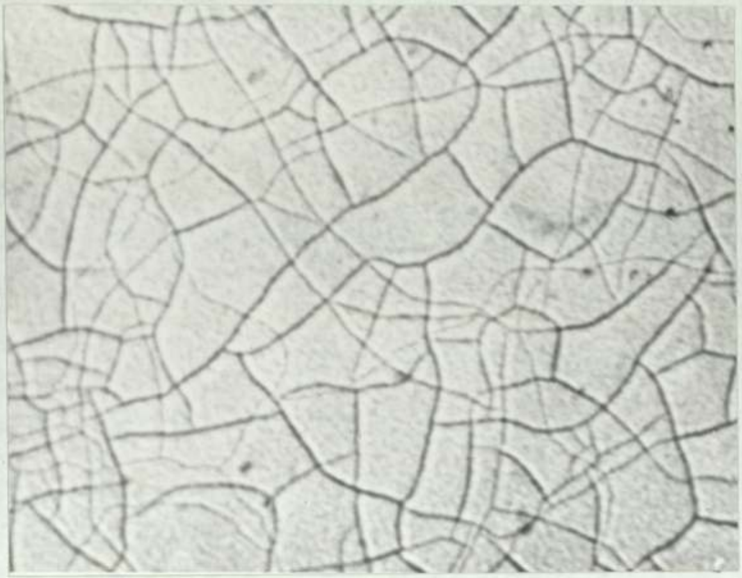

FIG. 4.2. 4.844 g/1 KF x 200

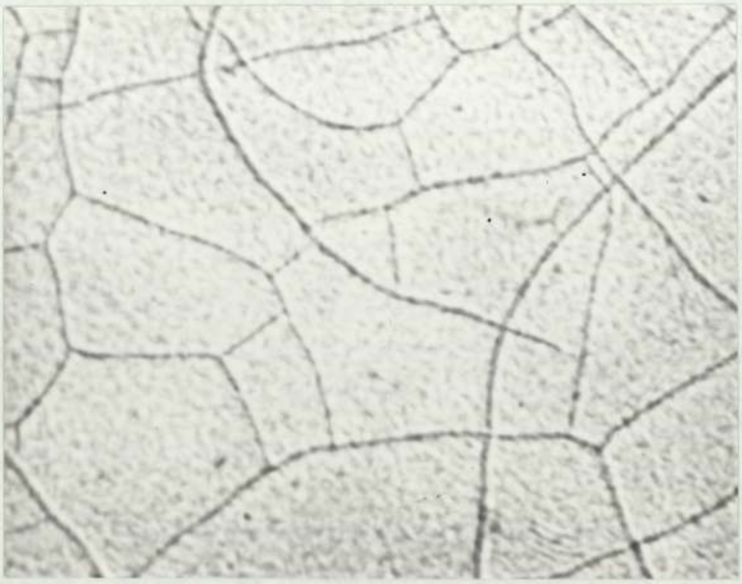

FIG. 4.3. 2.472 g/1 $(NH_4)_2SiF_6$ x 200

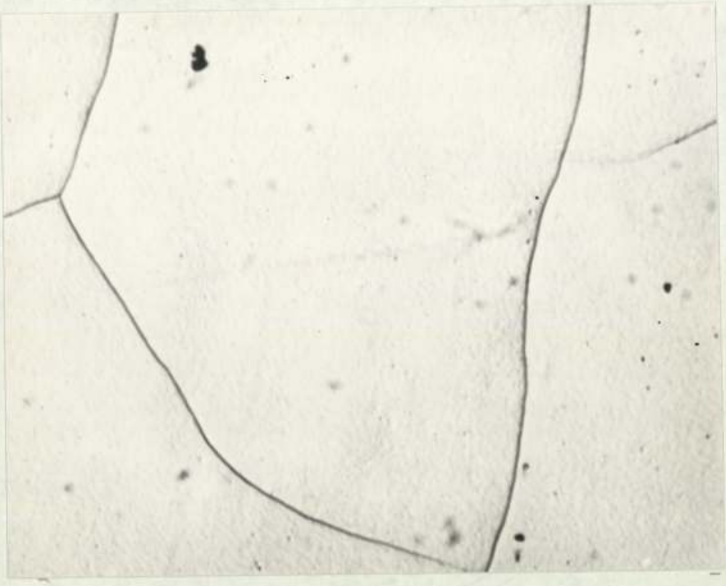

FIG. 4.4. 5.647 g/1 CsF x 200

FIG. 4.5. 1.0 g/1 H_2SiF_6 x 200

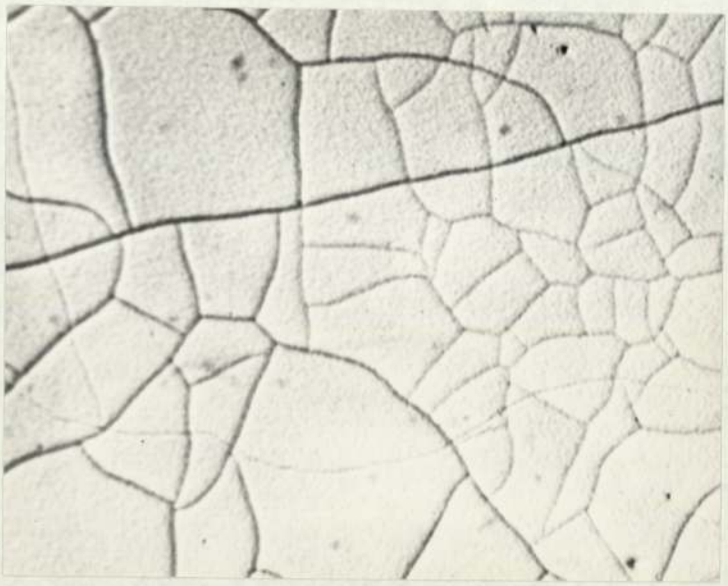

FIG. 4.6. 3.528 g/1 NH_4F x 200

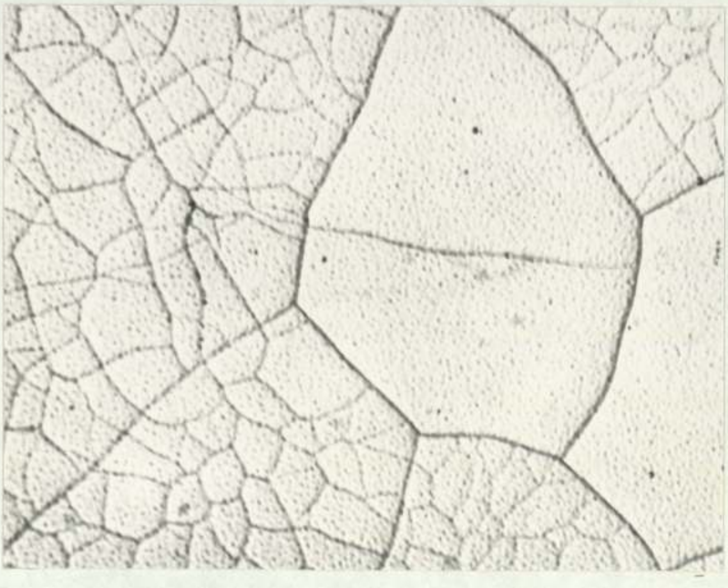

FIG. 4.7. 8.813 g/1 CsF x 200

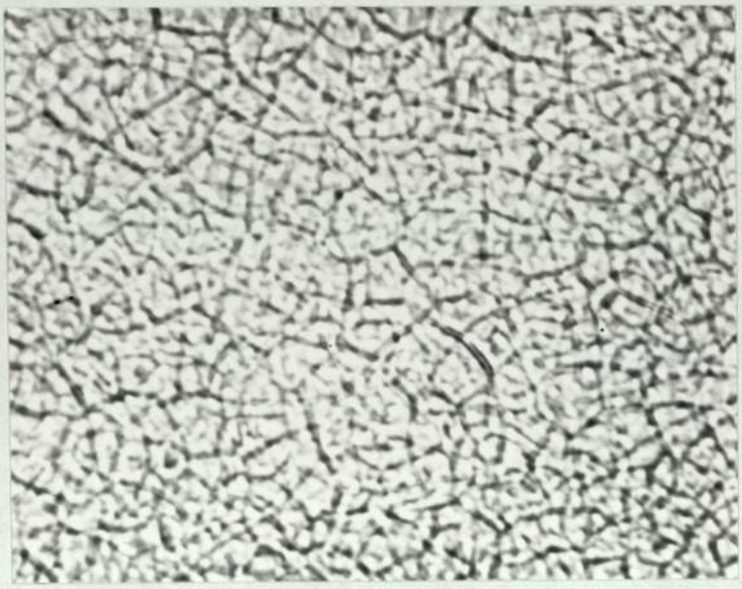

FIG. 4.8. 5.216 g/1 Na_2SiF_6 x 200

CHAPTER 5

GENERAL STATISTICAL METHODS

Various statistical methods[40,86,87,88] have been used for evaluating the experimental data and outlines of these are given below.

ARITHMETIC MEAN

A measure of the average value of a number of crack counts/10 mm is the arithmetic mean and is given by

$$\bar{x} = \frac{\Sigma x}{n}$$

where $\bar{x}$ = mean crack count in cracks/10 mm

and n = number of observations.

VARIANCE AND STANDARD DEVIATION

Measures of dispersion showing the degree of spread of the data about the average are the Variance and the Standard Deviation. The Variance of a Universe is the mean squared deviation of the items from the Universe mean. The best estimate of the Universe variance from experimental data is given by

$$V = \frac{\Sigma(x - \bar{x})^2}{n - 1}$$

The Standard Deviation is given by the square root of the Variance

$$S.D. = \sqrt{V}$$

The dimensions of the Standard Deviation are the same as those of the arithmetic mean $\bar{x}$ and it is therefore a more easily appreciated measure of dispersion. Furthermore since it is assumed that the samples are taken from a normally distributed population about 95% of the observations lie between $\bar{x} \pm 2$ Standard Deviations or more precisely 95.44% of the observations will lie between $\bar{x} \pm 2$ Standard Deviations.

DEGREES OF FREEDOM

In the relationship

$$V = \frac{\Sigma(x - \overline{x})^2}{(n - 1)}$$

the denominator (n - 1) represents the degrees of freedom of the Variance. It is the effective number of observations on which an estimate of the Variance is based and is not the same as the total number of observations. In this case one degree of freedom is used up in calculating the arithmetic mean. With large samples of about 50 or more the difference due to the use of either n or n - 1 is negligible but for small sample sizes the difference is important and in all cases n - 1 is the correct divisor.

NULL HYPOTHESIS

Where variations exist, such as the difference between the mean crack count on one cathode and another one, it is never possible to say definitely that any particular variation is not due to chance alone. By statistical analysis it is possible to state the odds against this and if these are high enough chance variations may be ruled out as the sole cause of the variation.

This is done by the Null Hypothesis procedure in which it is first assumed that there is no significant difference between the distributions being compared, that is they are drawn from the same population. The probability of the actual difference occurring due to chance alone is calculated and if this probability is very small the Null Hypothesis is rejected and the existence of a real difference is inferred. However it can never be formally proved that the Null Hypothesis is correct.

The choice of what is a low probability is arbitrary but evidence has been accumulated establishing certain levels of probability which give a reasonable assurance that wrong conclusions will seldom be drawn. The 5% level has been chosen such that with this probability, or less, the Null Hypothesis may be presumed false. This means that at the 5% level or less a deviation as large as or greater than the observed would be expected about once in every twenty trials due to chance variations alone, this low probability indicating a high degree of significance. It is important to note that the level of significance gives no guide to the magnitude of the effect, such as the size of the difference between two means.

STUDENTS t TEST

When comparing arithmetic means, such as mean crack count on one cathode with mean crack count on another one, the means are subject to some uncertainty because they have been estimated from a relatively small sample size. The t test allows for this uncertainty and is given by

$$t = \frac{\text{Error in mean}}{\text{Standard error of the mean}}$$

where Standard error of the mean $= \frac{\sigma}{\sqrt{n}}$

and σ = population standard deviation.

The test is applied to the Null Hypothesis that the two samples being compared are drawn from the same population and the probability is calculated of the difference $|\overline{x}_1 - \overline{x}_2|$ having a value as large as or greater than observed.

Since σ is not generally known an estimate of it must be calculated and one way of doing this is to utilise the standard deviations of the two samples $S.D._1$ and $S.D._2$ to calculate $(S.D._c)^2$, the combined variance

$$(S.D._c)^2 = \frac{(S.D._1)^2(n_1 - 1) + (S.D._2)^2(n_2 - 1)}{(n_1 - 1) + (n_2 - 1)}$$

The standard errors of the two means are given by

$$\frac{S.D._c}{\sqrt{n_1}} \text{ and } \frac{S.D._c}{\sqrt{n_2}}$$

and the standard error of the difference of means is

$$\sqrt{\frac{(S.D._c)^2}{n_1} + \frac{(S.D._c)^2}{n_2}} = z$$

$$\therefore \quad t = \frac{|\overline{x}_1 - \overline{x}_2|}{z}$$

The calculated value of t is then compared with percentage points in tables of the t-distribution for $(n_1 + n_2 - 2)$ degrees of freedom. Since the interest is in asking the question "is $\overline{x}_1$ significantly different from $\overline{x}_2$" and not if $\overline{x}_1 > \overline{x}_2$ or $\overline{x}_2 > \overline{x}_1$ then the test is two sided.

Students t test only shows if there is a difference between two means in a statistical sense; it gives no indication of the actual size of the difference.

VARIANCE RATIO

The F test or Variance Ratio is used to detect differences between two Variances and is the ratio of the greater Variance to the smaller one

$$F = \frac{V_1}{V_2} \quad \text{where} \quad V_1 > V_2$$

Associated with F are the degrees of freedom on which V_1 and V_2 are based.

Before comparing two means by the t-test it is necessary to compare the two Variances of the data from which the two means were calculated. This is done by the F test and should any significant difference be found between them then they are not drawn from the same Universe and it is then not correct to use the t-test for comparing the means.

LINEAR REGRESSION AND CORRELATION

This is the linear dependence of one variable Y on another variable X, the dependent variable being denoted by Y and the independent one by X. For example, crack counts/10 mm are always taken as the dependent variable Y, the independent variable X being some other measurement such as the distance in mm from the bottom of a cathode.

More complex relationships were investigated between crack counts/10 mm as the dependent variable and current densities together with fluoride concentrations as independent variables for Hull Cell results. Curvilinear multiple regression methods were used for this analysis and will be discussed later.

For simple linear regression the experimental points may be plotted on linear graph paper with the dependent variable Y on the vertical axis and the independent one X on the horizontal axis. The best straight line through these points is the regression line of Y on X and is of the form

$$Y = m x + c$$

The capital Y denotes a predicted or mean value of the dependent variable and the small x denotes an observed value of the independent variable, c and m being constants. The method of estimating c and m is by The Method of Least Squares. This consists of finding values of m and c that make the sum of squares of the deviations of the observed values of Y from the line a minimum and the line satisfying these requirements passes through the mean of all the observations.

If the observations are denoted by

$$(x_1y_1),\ (x_2y_2),\ \ldots\ldots\ (x_ny_n)$$

the equation of the line is

$$Y = \overline{y} + m(x - \overline{x})$$

where $\overline{y}$ = mean of $y_1,\ y_2,\ \ldots\ldots\ y_n$

$\overline{x}$ = mean of $x_1,\ x_2,\ \ldots\ldots\ x_n$

$$m = \frac{\Sigma(x - \overline{x})(y - \overline{y})}{\Sigma(x - \overline{x})^2}$$

The correlation coefficient r is a measure of the goodness of fit of the calculated regression equation to the experimental points and is given by

$$r = \frac{\Sigma(x - \overline{x})(y - \overline{y})}{\sqrt{\Sigma(x - \overline{x})^2\Sigma(y - \overline{y})^2}}$$

The correlation coefficient r always lies between -1 and +1, when it is is positive one variable tends to increase as the other increases when it is negative one variable tends to decrease as the other increases. When the value of r is unity the variables fall in a straight diagonal line and the relationship is perfect. When r is equal to zero the points scatter in all directions and the variables are independent.

The significance of the correlation coefficient may be assessed directly from tables which give values of correlation coefficients for different significance levels. The appropriate degrees of freedom are given by (n - 2) where n is the number of points.

METHOD OF CALCULATION

The various formulae given above are not necessarily in the best form to use for numerical calculations. Most of the calculations were done using an Olivetti Desk Computer utilising standard programmes.

CHAPTER 6

RESULTS AND DISCUSSIONS ON FIXED CURRENT DENSITY CATHODES

RESULTS OF CRACK COUNTS ON 75 mm x 50 mm CATHODES

Horizontal crack counts 25 mm from the bottom of the cathode are given together with the amount of fluoride compound in g/l, the equivalent amount of fluorine in g/l, the means and standard deviations of the crack counts/10 mm together with the number of readings used in calculating them.

For vertical crack counts/10 mm either linear regression analysis results or means and standard deviations are given. In a few cases only the means, standard deviations and linear regression analysis results are given, all calculated on the same data. Regression results are tabulated first, giving the equivalent amount of fluorine in g/l of the fluoride compound followed by the slope, the intercept, the correlation coefficient, the number of readings used in the calculations together with the percentage probability. Then follows the means and standard deviations ending with the number of readings used for calculating them.

In the regression analysis the dependent variable is cracks/10 mm and the independent one is the distance in mm from the bottom of the cathode.

KEY TO ABBREVIATIONS USED IN THE TABLES

g/l = gms/litre

$\bar{x}$ = mean crack count in cracks/10 millimetres

S.D. = Standard Deviation

Number = number of results

m = slope of the linear equations $Y = mx + c$

c = intercept of the linear equation $Y = mx + c$

r = correlation coefficient

% prob. = percentage probability

ϕ = degrees of freedom

TABLE 6.1

FIXED CURRENT DENSITY RESULTS

LITHIUM FLUORIDE ADDITIONS

Glass Container, horizontal crack count

Added LiF g/l	Calculated F^- g/l	Calculated $\bar{x}$	Calculated S.D.	Number	Comments
1.237	0.906	-	-	-	No cracking
1.854	1.358	125	22.4	20	
2.471	1.810	1969	-	-	$\bar{x}$ estimated
2.780	2.036	1969	-	-	$\bar{x}$ estimated

Glass container, vertical crack count

Linear Regression					Means and Standard Deviations		
Calculated F^- g/l	Calculated m	Calculated c	Calculated r	Number and % Prob.	Calculated $\bar{x}$	Calculated S.D.	Number
0.906	-	-	-	No cracking	-	-	No cracking
1.358	4.4	23.1	0.916	55, 0.1	-	-	-
1.810	72.7	274.4	0.991	18, 0.1	1772	-	$\bar{x}$ estimated
2.036	63.5	799.2	0.852	12, 0.1	1476	-	$\bar{x}$ estimated

LITHIUM FLUOROSILICATE ADDITIONS

Plastic container, horizontal crack count

Added Li_2SiF_6 g/l	Calculated F^- g/l	Calculated $\overline{x}$	Calculated S.D.	Number	Comments
1.081	0.790	14	17.8	20	
1.622	1.186	220	169.6	20	zoning
2.162	1.580	429	72.6	20	
2.703	1.976	446	76.6	20	
3.243	2.372	530	93.0	20	
4.324	3.160	912	100.8	20	
6.486	4.740	-	-	-	Chromium, no cracking

Plastic container, vertical crack count

Linear Regression					Means and Standard Deviations		
Calculated F^- g/l	Calculated m	Calculated c	Calculated r	Number and % Prob.	Calculated $\overline{x}$	Calculated S.D.	Number
0.790	-	-	-	-	22	23.4	32
1.186	-	-	-	-	131	95.6	31
1.580	-3.4	593.2	-0.607	26, 0.1	510	84.1	26
1.976	-10.3	813.8	-0.844	23, 0.1	362	56.7	5
2.372	-13.2	1019.5	-0.946	23, 0.1	411	61.8	5
3.160	4.9	636.8	0.753	23, 0.1	770	109.2	29
4.740	-	-	-	Chromium, no cracking	-	-	Chromium, no cracking

SODIUM FLUORIDE ADDITIONS

Glass container, horizontal crack count

Added NaF g/l	Calculated F^- g/l	Calculated $\bar{x}$	Calculated S.D.	Number	Comments
2.5	1.131	15	8.7	20	
3.0	1.358	123	38.3	20	
3.5	1.584	588	49.2	20	
3.75	1.697	1107	70.1	20	
4.0	1.810	-	-	-	No chromium

Glass container, vertical crack count

Linear Regression					Means and Standard Deviations		
Calculated F^- g/l	Calculated m	Calculated c	Calculated r	Number and % Prob.	Calculated $\bar{x}$	Calculated S.D.	Number
1.131	-	-	-	-	19	10.0	38
1.358	5.1	16.7	0.909	57, 0.1	-	-	-
1.584	18.7	115.7	0.962	44, 0.1	-	-	-
1.697	35.7	365.1	0.902	27, 0.1	1476	-	$\bar{x}$ estimated
1.810	-	-	-	No chromium	-	-	No chromium

SODIUM FLUOROSILICATE ADDITIONS

Plastic container, horizontal crack count

Added Na_2SiF_6 g/l	Calculated F^- g/l	Calculated $\bar{x}$	Calculated S.D.	Number	Comments
1.304	0.790	18	15.1	20	
2.608	1.580	52	21.1	20	
5.216	3.160	661	79.1	20	
7.824	4.740	-	-	-	Chromium, no cracking

Plastic container, vertical crack count

Linear Regression					Means and Standard Deviations		
Calculated F^- g/l	Calculated m	Calculated c	Calculated r	Number and % Prob.	Calculated $\bar{x}$	Calculated S.D.	Number
0.790	-	-	-	-	14	14.8	29
1.580	-	-	-	-	85	48.1	30
3.160	-19.5	1202	-0.753	16, 0.1	910	238.2	16
4.740	-	-	-	Chromium no cracking	-	-	Chromium no cracking

POTASSIUM FLUORIDE ADDITIONS

Glass container, horizontal crack count

Added KF g/l	Calculated F^- g/l	Calculated $\bar{x}$	Calculated S.D.	Number	Comments
2.768	0.906	-	-	-	No cracking
3.460	1.131	18	13	20	
4.152	1.358	41	14	20	
4.844	1.584	215	64	20	
5.536	1.810	901	50	20	
6.228	2.036	1181	-	-	$\bar{x}$ estimated
6.920	2.264	984	-	-	$\bar{x}$ estimated
7.612	2.489	-	-	-	No chromium

Glass container, vertical crack count

Linear Regression					Means and Standard Deviations		
Calculated F^- g/l	Calculated m	Calculated c	Calculated r	Number and % Prob.	Calculated $\bar{x}$	Calculated S.D.	Number
0.906	-	-	-	No cracking	-	-	No cracking
1.131	-	-	-	-	10	10.6	55
1.358	-	-	-	-	46	20.4	55
1.584	6.5	55.0	0.931	28, 0.1	-	-	-
1.810	34.2	181.4	0.975	24, 0.1	1271	154.0	14
2.036	79.3	67.9	0.990	14. 0.1	1198	93.0	8
2.264	77.2	-39.3	0.970	11, 0.1	709	-	$\bar{x}$ estimated
2.489	-	-	-	No chromium	-	-	No chromium

POTASSIUM FLUOROSILICATE ADDITIONS

Plastic container, horizontal crack count

Added K_2SiF_6 g/l	Calculated F^- g/l	Calculated $\bar{x}$	Calculated S.D.	Number	Comments
1.529	0.790	-	-	-	Chromium, no cracking
3.058	1.580	293	67.9	20	
6.116	3.160	681	58.1	13	
9.114	4.740	700	35.9	13	
12.232	6.320				Chromium, no cracking

Plastic container, vertical crack count

Linear Regression					Means and Standard Deviations		
Calculated F^- g/l	Calculated m	Calculated c	Calculated r	Number and % Prob.	Calculated $\bar{x}$	Calculated S.D.	Number
0.790	-	-	-	Chromium, no cracking	-	-	Chromium no cracking
1.580	-4.8	480.6	-0.699	28, 0.1	352	110.1	28
3.160	-3.8	870.1	-0.414	16, 5/10	795	133.8	16
4.740	-7.8	1020.3	-0.731	13, 0.1	709		$\bar{x}$ estimated
6.320	-	-	-	Chromium no cracking	-	-	Chromium no cracking

RUBIDIUM FLUORIDE ADDITIONS

Glass container, horizontal crack count

Added RbF g/l	Calculated F^- g/l	Calculated $\bar{x}$	Calculated S.D.	Number	Comments
1.333	0.242	-	-	-	No cracking
2.666	0.484	-	-	-	No cracking
6.666	1.212	128	40.4	40	

Glass container, vertical crack count

Linear Regression					Means and Standard Deviations		
Calculated F^- g/l	Calculated m	Calculated c	Calculated r	Number and % Prob.	Calculated $\bar{x}$	Calculated S.D.	Number
0.242	-	-	-	No cracking	-	-	No cracking
0.484	-	-	-	No cracking	-	-	No cracking
1.212	4.3	37.8	0.861	55, 0.1	-	-	-

CAESIUM FLUORIDE ADDITIONS

Glass container, horizontal crack count

Added CsF g/l	Calculated F^- g/l	Calculated $\bar{x}$	Calculated S.D.	Number	Comments
1.809	0.226	-	-	-	No cracking
4.037	0.505	5	8.7	20	
5.647	0.706	35	14.1	20	
7.234	0.906	507	62.0	17	
8.813	1.102	1181	-	-	$\bar{x}$ estimated
10.547	1.318	-	-	-	No chromium
12.860	1.608	-	-	-	No chromium

Glass container, vertical crack count

Linear Regression					Means and Standard Deviations		
Calculated F^- g/l	Calculated m	Calculated c	Calculated r	Number and % Prob.	Calculated $\bar{x}$	Calculated S.D.	Number
0.226	-	-	-	No cracking	-	-	No cracking
0.505	-	-	-	-	9	9.9	60
0.706	-	-	-	-	21	20.8	51
0.906	12.1	171.3	0.928	38, 0.1	637	48.2	11
1.102	46.3	387.4	0.971	18, 0.1	1181	-	$\bar{x}$ estimated
1.318	-	-	-	No chromium	-	-	No chromium
1.608	-	-	-	No chromium	-	-	No chromium

CAESIUM FLUOROSILICATE ADDITIONS

Plastic container, horizontal crack count

Added $CsSiF_6$ g/l	Calculated F^- g/l	Calculated $\bar{x}$	Calculated S.D.	Number	Comments
2.831	0.790	14	17.8	20	
5.662	1.580	293	77.9	20	
7.520	2.102	385	83.9	20	
11.324	3.160	168	38.2	20	

Plastic container, vertical crack count

Linear Regression					Means and Standard Deviations		
Calculated F^- g/l	Calculated m	Calculated c	Calculated r	Number and % Prob.	Calculated $\bar{x}$	Calculated S.D.	Number
0.790	-	-	-	-	14	19.3	31
1.580	-11.0	640.1	-0.775	24, 0.1	-	-	-
2.102	-15.9	917.8	-0.665	14, 1/0.1	372	34.8	14
3.160	1.1	111.7	0.411	27, 5/10	139	40.3	27

AMMONIUM FLUORIDE ADDITIONS

Glass container, horizontal crack count

Added NH_4F g/1	Calculated F^- g/1	Calculated $\bar{x}$	Calculated S.D.	Number	Comments
1.762	0.906	-	-	-	About 10 cracks only on panel
2.205	1.131	22	11.1	40	
2.646	1.358	61	26.5	40	
3.087	1.584	158	27.3	40	
3.528	1.810	549	128.6	40	
4.410	2.264	-	-	-	No chromium deposit
5.292	2.715	-	-	-	" " "

Glass container, vertical crack count

Linear Regression					Means and Standard Deviations		
Calculated F^- g/1	Calculated m	Calculated c	Calculated r	Number and % Prob.	Calculated $\bar{x}$	Calculated S.D.	Number
0.906	-	-	-	-	-	-	-
1.131	-	-	-	-	21	13.7	54
1.358	-	-	-	-	51	24.8	50
1.584	6.4	13.4	0.932	55, 0.1	189	107.7	55
1.810	19.6	140.2	0.951	39, 0.1	897	65.1	22
2.264	-	-	-	No chromium	-	-	No chromium
2.715	-	-	-	No chromium	-	-	No chromium

AMMONIUM FLUOROSILICATE ADDITIONS

Plastic container, horizontal crack count

Added $(NH_4)_2SiF_6$ g/l	Calculated F^- g/l	Calculated $\bar{x}$	Calculated S.D.	Number	Comments
1.236	0.790	34	27.1	20	
2.472	1.580	147	43.4	20	
3.708	2.372	369	72.2	20	
4.944	3.160	800	48.6	17	
7.416	4.740	-	-	-	Chromium, no cracking

Plastic container, vertical crack count

Linear Regression					Means and Standard Deviations		
Calculated F^- g/l	Calculated m	Calculated c	Calculated r	Number and % Prob.	Calculated $\bar{x}$	Calculated S.D.	Number
0.790	-	-	-	-	45	25.2	28
1.580	-7.9	416.8	-0.754	25, 0.1	228	153.6	25
2.372	-27.1	932.7	-0.925	13, 0.1	309	42.2	11
3.160	5.1	626.7	-0.826	26, 0.1	750	94.4	26
4.740	-	-	-	Chromium no cracking	-	-	no cracking

HYDROFLUOSILICIC ACID ADDITIONS

Plastic container, horizontal crack count

Added H_2SiF_6 g/l	Calculated F^- g/l	Calculated $\bar{x}$	Calculated S.D.	Number	Comments
0.5	0.395	-	-	-	Chromium, no cracking
1.0	0.790	11	16.0	40	
2.0	1.580	737	62.6	20	
3.0	2.372	850	-	-	$\bar{x}$ estimated
4.0	3.160	1065	-	-	$\bar{x}$ estimated
5.0	3.950	-	-	-	Chromium, no cracking

Plastic container, vertical crack count

Linear Regression					Means and Standard Deviations		
Calculated F^- g/l	Calculated m	Calculated c	Calculated r	Number and % Prob.	Calculated $\bar{x}$	Calculated S.D.	Number
0.395	-	-	-	Chromium no cracking	-	-	Chromium no cracking
0.790	-	-	-	-	23	23.3	60
1.580	-	-	-	-	635	98.8	51
2.372	-	-	-	-	850	-	$\bar{x}$ estimated
3.160	-	-	-	-	1063	-	$\bar{x}$ estimated
3.950	-	-	-	Chromium no cracking	-	-	Chromium no cracking

DISCUSSION OF CRACK COUNTS ON 75 mm x 50 mm CATHODES

HORIZONTAL CRACK COUNTS

It was found experimentally that the chromium plating base solution without any fluoride addition did not deposit chromium, neither did deposition occur at high fluoride concentrations of about 10 g/l.

At the lower concentrations of fluorides of about 1 g/l skew distributions of crack counts were observed. Statistically about 95% of the population should lie within $\bar{x} \pm 2$ standard deviations and for lithium fluorosilicate at 0.790 gms/litre fluoride this was $14 \pm (2 \times 17.8) = -22$ to $+50$. Since it is physically impossible to have a negative crack count the distribution can be assumed skew. Similar distributions at the lower crack counts were shown in the majority of cases.

At low fluoride concentrations chromium deposition occurred with no cracking and then cracking commenced as the fluoride concentration increased, increasing with greater fluoride concentration. At some of the higher fluoride concentrations such as with potassium fluoride and caesium fluorosilicate the crack counts became less. In other cases such as lithium fluorosilicate, sodium fluorosilicate, potassium fluorosilicate, ammonium fluorosilicate and hydrofluosilicic acid cracking ceased at the higher fluoride concentrations although chromium was still deposited. With excess fluorides chromium deposition ceased in all cases.

Although all the above conditions were not found with every fluoride used it was assumed that they would have been had the correct fluoride concentrations been used.

The following hypothesis was therefore made. As the concentration of fluoride was slowly increased from zero the following changes occurred. Initially there was no chromium deposit followed by a chromium deposit with no cracking, cracking then began and increased to a maximum finally falling to zero cracking followed by crack free chromium deposition. Finally at the highest fluoride concentrations chromium ceased altogether. This is summarised in Fig. 6.1.

In this qualitative approach no account was taken of the different fluorides although it was noticed that simple ones gave different microcracking effects from complex fluorides.

The complex fluorides caused cracking at lower fluoride concentrations than the simple ones in the cases of lithium and ammonium, the reverse probably being true in the other cases. It is not possible to say if simple or complex fluorides caused more cracking at the lower concentrations on the evidence available. At the highest concentrations the situation was much more clear. At equivalent fluoride concentrations the simple fluorides gave much higher crack counts in all cases. The simple fluorides were also more effective in stopping either cracking or chromium deposition at the higher concentrations as in the cases of sodium, potassium, caesium and ammonium, lithium also following the same pattern.

There were thus differences between the effects of simple and complex fluorides which were not due to fluoride concentration alone. Other aspects of the molecule appeared to have influenced cracking and will be considered later.

The simple fluorides caused about twice as many cracks/10 mm as the complex fluorides; ammonium was exceptional in that the complex fluoride caused the greatest cracking. Because of the differences between the effects of simple and complex fluorides they must be considered separately.

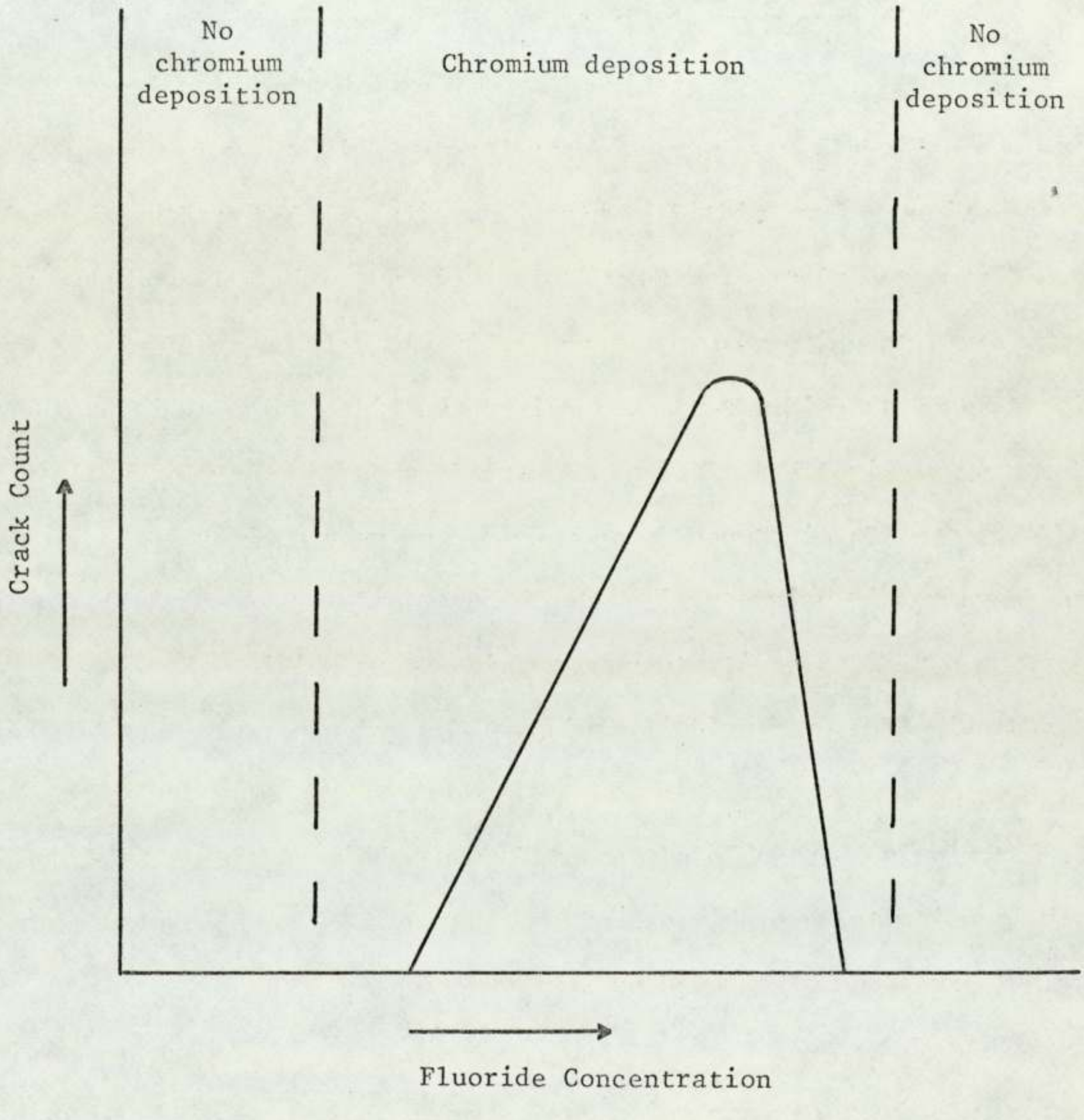

FIG. 6.1. General Effects of Fluorides

VERTICAL CRACK COUNTS

Unlike the horizontal ones these were best analysed by linear regression in the majority of cases, with crack counts/10 mm as the dependent variable and distance in millimetres from the bottom of the cathode as independent variable. In some cases means and standard deviations of crack counts/10 mm were also calculated.

Out of a total of twenty-nine regression equations calculated twenty-seven of them were significant at the 0.1% level and two between 5% and 10%; the results were therefore statistically very significant there being linear relationships between the two variables. Occasionally results were best analysed by both linear regression and calculation of means and standard deviations. That is when the rate of change of crack count with vertical distance up the cathode became approximately zero regression analysis was discontinued and the means together with standard deviations calculated on the remainder of the data. In a few cases linear regression analysis, means and standard deviations were all calculated for the same results. These are the ones with the number of results the same in both linear regression; and means and standard deviations calculations.

One striking difference between the effects of simple and complex fluorides was that simple fluorides gave higher crack counts the further up the cathode counting was done. That is the regression equations all had positive slopes, the reverse being shown with complex fluorides. This was confirmatory evidence of the different effects of simple and complex fluorides.

In the case of the simple fluorides the slopes of the regression equations increased with increasing fluoride concentration and this was also shown with the complex fluorides but in a negative sense, although in this case the change was not so marked. At some of the

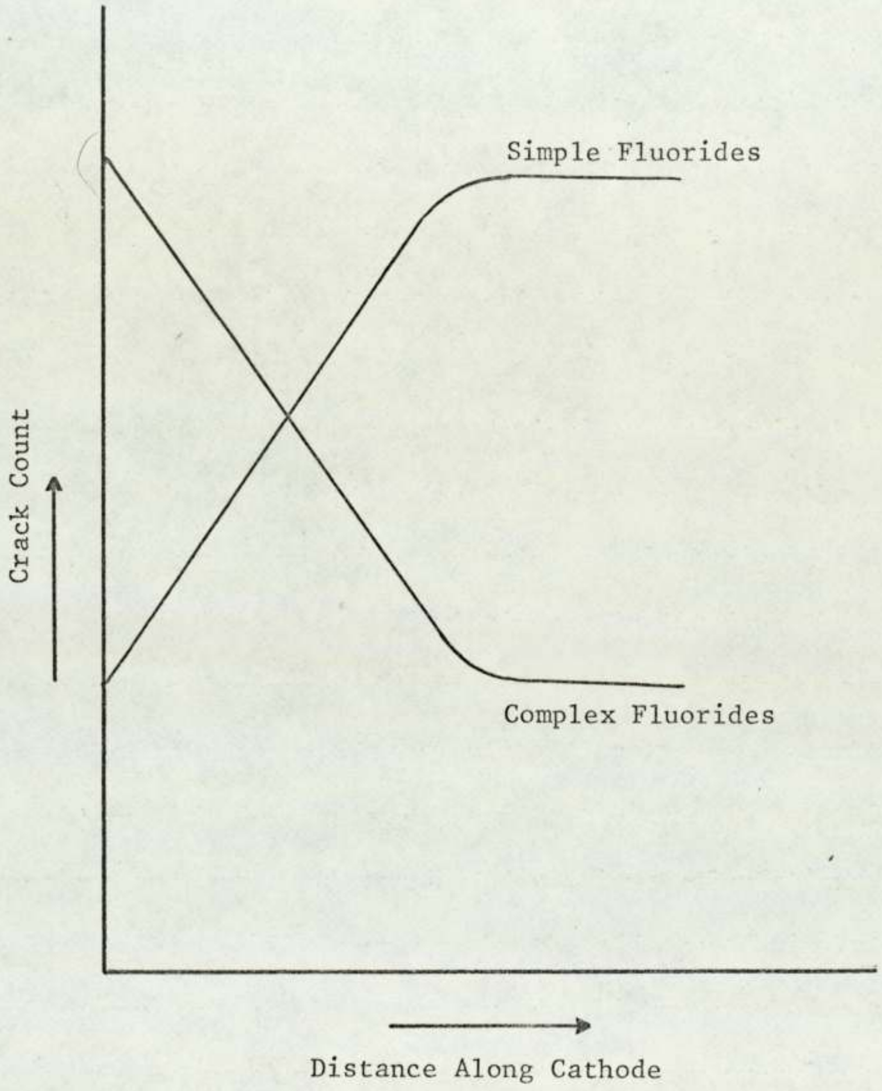

FIG. 6.2. The Effects of Simple and Complex Fluorides on Microcracking

highest concentrations this general pattern was not followed, with lithium fluorosilicate for example, the sign of the slope changed from negative to positive as was also the case with caesium fluorosilicate and ammonium fluorosilicate. These occurred very near the concentrations where chromium deposition either ceased or cracking stopped and therefore could be considered as edge effects.

In general the cracks showed the following approximate patterns particularly at the higher concentrations (Fig. 6.2).

QUANTITATIVE ANALYSIS OF HORIZONTAL CRACK COUNTS

Linear regression analysis was done on the data for each of the fluorides in turn, the horizontal mean crack count, $\bar{x}$, being taken as the dependent variable and the fluoride concentration as the independent variable (Table 6.2).

The correlation coefficients r were only significant at the 10% level in five cases, between 5% and 10% in three cases and 5% or less in three cases. Although some of the correlation coefficients were not significant at 5% they were not unreasonably so and they were also based on only a few degrees of freedom. It was therefore considered statistically possible to proceed further with the analysis.

Examination of the slopes, m, showed that for the simple fluorides these decreased from lithium down to potassium with an increase for caesium. Similarly for the complex fluorides these decreased from hydrogen down to potassium with an increase for caesium. The results for ammonium were not taken into consideration because ammonium, NH_4, cannot be pleased in the same vertical column of the periodic table as the alkali metals and direct comparison of results should not therefore be made.

The apparently anomalous behaviour of caesium cannot be explained in the same way as for NH_4 and there was further confirmatory evidence

TABLE 6.2

DERIVED RESULTS

	LiF	NaF	KF	CsF
m	2915.9	1853.4	1127.4	2006.0
c	-3703.8	-2215.2	-1356.8	-1182.3
r	0.945	0.932	0.914	0.938
ϕ	1	2	4	2
% Prob.	10	5-10	1	5-10
	Li_2SiF_6	Na_2SiF_6	K_2SiF_6	Cs_2SiF_6
m	347.7	287.6	128.8	288.5
c	-216.0	-286.5	151.0	-199.3
r	0.979	0.959	0.886	0.986
ϕ	4	1	1	1
% Prob.	0.1	10	10	10
	NH_4F	$(NH_4)_2SiF_6$	H_2SiF_6	
m	741.7	318.9	413.7	
c	-893.3	-292.4	-152.0	
r	0.898	0.962	0.924	
ϕ	2	2	2	
% Prob.	10	5	5-10	

of this behaviour. For caesium fluoride additions cracking ceased at a fluoride concentration of 1.318 g/l, for caesium fluorosilicate crack counts dropped from a previous value of 385 to 168 cracks/10 mm at a concentration of 3.160 g/l fluoride. For the other fluorides cracking ceased at about double the fluoride concentrations of caesium fluoride and fluorosilicate.

The caesium fluorides stopped cracking at about the same concentration at which the other fluorides began to cause cracking, the exceptions being ammonium fluorosilicate and hydrofluosilicic acid. The caesium fluorides were more efficient cracking catalysts at lower fluoride concentrations than other fluorides and also inhibited cracking at lower fluoride concentrations than other fluorides.

In other words both caesium fluoride and caesium fluorosilicate were more effective catalysts than the other fluorides at equivalent fluoride concentrations.

Returning to the derived results, lithium, sodium and potassium fluorides were placed in one group and the complex fluorides of (hydrogen), lithium, sodium and potassium in a second group. Results for caesium and ammonium were not included for the reasons already given.

Linear regression analysis was done on the data for each of the two groups. The slopes m, i.e. a measure of the rate of change of crack count with fluoride concentration, were taken as the dependent variables with a blanket coverage of various parameters of the alkali metals taken in turn as the independent variables (Table 6.3).

In view of the small number of degrees of freedom, either two or three, and the fact that the independent variables can all be taken as some measure of the same property i.e. atomic, it is reasonable to extent the probability from the 5% level to the 10% level. Then linear relationships exist between a measure of the rate of change of crack count with fluoride concentration and various parameters of the alkali metals. For the simple fluorides these are atomic number, atomic weight, atomic radius, cube edge and melting point and for complex fluorides these are atomic number, atomic weight, ionic radius and ionisation potential.

Since relationships exist for both simple and complex fluorides for atomic number and atomic weight with correlation coefficients at the 5% level or less it is considered that the alkali metal influences microcracking. These results are illustrated graphically (Fig. 6.3 and Fig. 6.4).

The information listed in Tables 6.4 and 6.5 has been obtained from several sources[61,77,81,82,83,84,85].

With the exception of atomic numbers and atomic weights there are some discrepancies in the published data. All the data is not available from any one reference and in two cases there are obvious errors[83,84]. It was, therefore, decided to take a series of results, such as atomic radius, from a single reference.

Ionisation potential[83] is the work in electron volts required to move a given electron from its atomic orbit and place it at rest at an infinite distance.

Atomic radius[83] is the radius of the volume occupied by an atom. This volume in many cases approximates to a distorted sphere.

Ionic radius[83] of the same species of atom will be somewhat less or greater than atomic radius because the outermost shell of electrons has either been stripped off or increased in the formation of the ion.

TABLE 6.3

REGRESSION ANALYSIS OF DERIVED RESULTS

Independent Variable	Type of Fluoride	Correlation Coefficient	% Prob.
Atomic number	Simple	- 0.994	5
Atomic weight	Simple	- 0.994	5
Atomic radius	Simple	- 0.986	10
Ionic radius	Simple	- 0.965	below 10
Ionisation potential	Simple	0.920	below 10
Cube edge	Simple	- 0.990	5-10
Melting point	Simple	0.990	5-10
Boiling point	Simple	0.972	below 10
Atomic number	Complex + hydrogen	- 0.979	2
Atomic weight	Complex + hydrogen	- 0.981	2
Atomic radius	Complex	- 0.981	below 10
Ionic radius	Complex	- 0.995	5
Ionisation potential	Complex	0.999	2
Cube edge	Complex	- 0.976	below 10
Melting point	Complex	0.876	below 10
Boiling point	Complex	0.825	below 10

TABLE 6.4

Property	Li	Na	K	Rb	Cs
Atomic number	3	11	19	37	55
Atomic weight	7	23	39	85	133
Atomic radius cms 10^{-8}	1.56	1.86	2.23	2.36	2.55
Ionic radius cms 10^{-8}	0.78	0.98	1.33	1.49	1.65
Length of unit cube cell edge cms 10^{-8}	3.50	4.30	5.20	5.62	6.05
m.p. °C 760 mm Hg	180	98	66	39	29
b.p. °C 760 mm Hg	1400	878	757	696	670
Ionisation potential eV	5.39	5.14	4.34	4.18	3.89

TABLE 6.5

Solubility in gms/100 ml water 18°C				
LiF 0.27	NaF 4.22	KF 92	RbF 131	CsF 367
Li_2SiF_6 73	Na_2SiF_6 0.65	K_2SiF_6 0.12	Rb_2SiF_6 0.16	Cs_2SiF_6 0.60
H_2SiF_6 very soluble	NH_4F 100	$(NH_4)_2SiF_6$ 17		

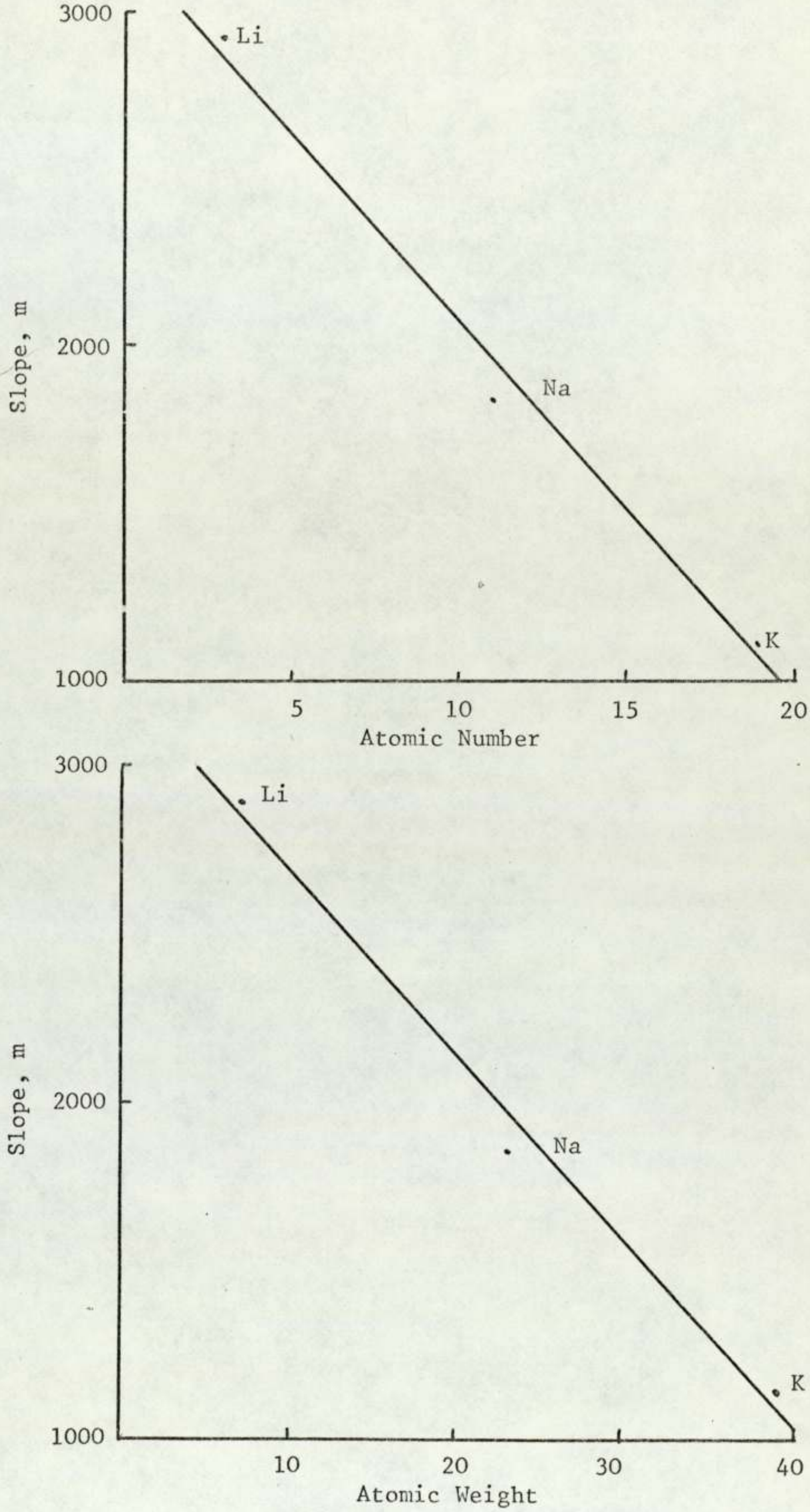

FIG. 6.3. Regression Analysis for Simple Fluorides

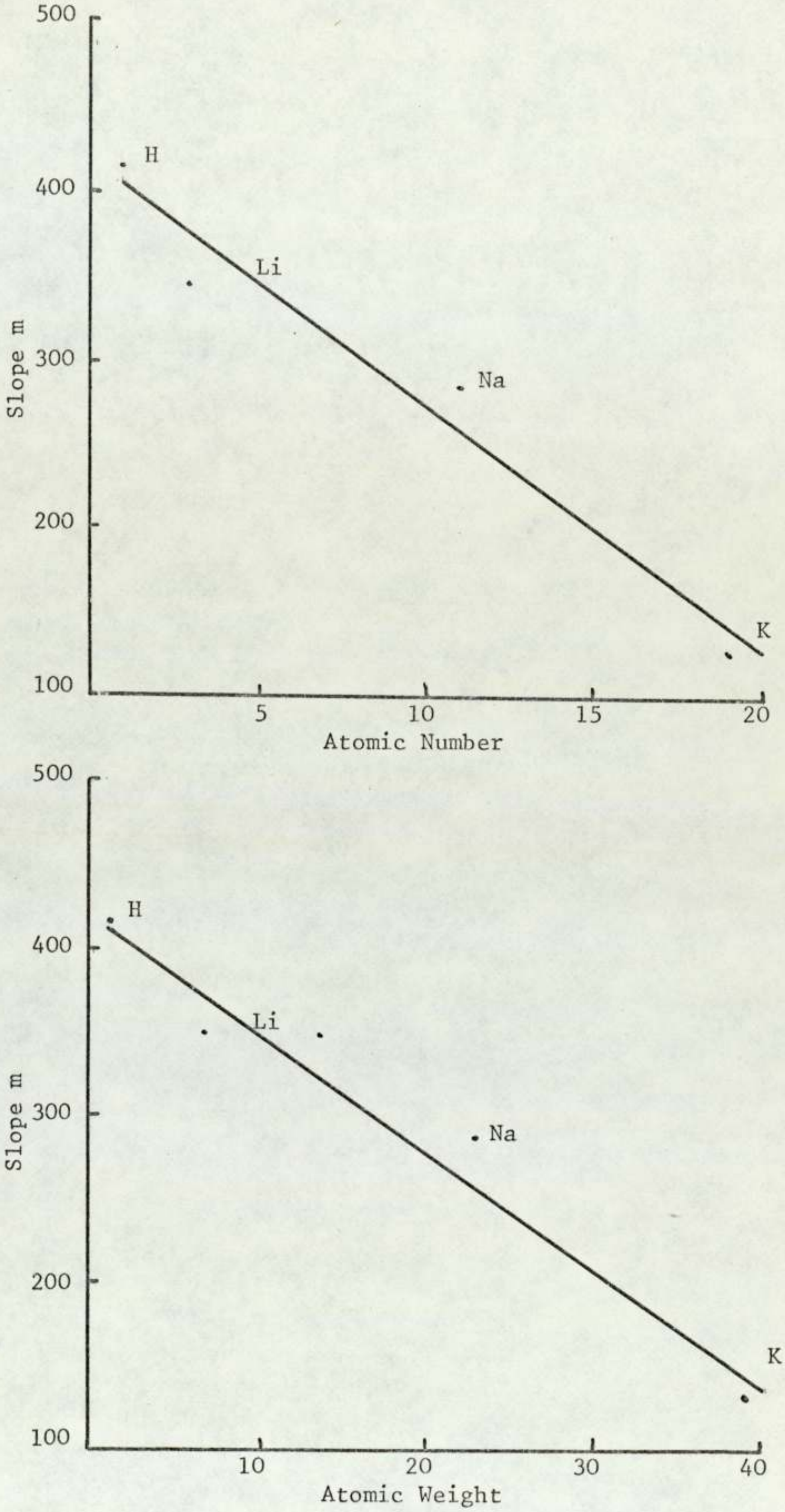

FIG. 6.4. Regression Analysis for Complex Fluorides

Conclusions drawn from this analysis were:

(1) Microcracking was not only related to fluoride concentration but also to the particular fluoride used. Quantitative relationships exist between some measurement of the alkali metal atom or hydrogen atom involved and the rate of change of crack count with fluoride concentration.

(2) Caesium was apparently anomalous and did not follow the general pattern and was a much more efficient alkali metal than the others with respect to microcracking.

(3) The ammonium ion catalysts although following the same general pattern were not included in the analysis because of the differences between ammonium ion and the alkali metals.

EFFECT OF CONTAINER ON THE FLUORIDE CATALYST

It was found during initial experimental work that the age of the chromium plating solution influenced microcracking. The only bath constituents that were likely to change markedly over so short a time period of a few hours were reduced chromium and the fluoride catalyst reacting with glass.

Potassium fluoride was chosen as the catalyst to investigate because potassium is half way down the alkali metal series. A concentration of 4.844 g/l potassium fluoride was used to give a crack count of about 200 cracks/10 mm since any reasonable change in crack count would easily be shown up.

Ten minutes before each of the plating times given the steel working cathode was replaced with a freshly bright nickel plated one. This new cathode was replaced by the working cathode, which was stored in water, after ten minutes plating.

Crack counts were done on the ten minute cathodes, horizontally 25 mm from the bottom.

A non cracked chromium deposit was obtained from this solution when used in a polythene beaker. The same solution when transferred to a glass beaker gave a microcracked deposit and the results are tabulated in Table 6.6.

Since the effect of transferring the solution from a polythene to a glass container caused cracking it was inferred that the cracking was caused by a reaction product of potassium fluoride and glass. To test this other fluorides were added to chromium plating solutions in polythene containers with the following results (Table 6.7).

No substantial cracking occurred in any of the above cases but fresh solutions of the same composition caused cracking when used in glass containers under otherwise identical conditions. An increase in the time of chromium plating from the standard ten minutes to approximately sixty minutes in the case of 4.844 g/l potassium fluoride resulted in some cracking, when in a plastic container only. It was difficult to accurately count the cracks because of surface roughness but the general pattern was not that of a microcracked deposit.

To simulate the effects of a lead lined tank used in industrial practice a lead lining was placed in a polythene container containing a fresh plating solution with 4.844 g/l potassium fluoride. After plating under standard conditions for ten minutes no cracking was found in the deposit.

Since it was established that under the plating conditions used microcracking was caused by a reaction product it was assumed that this product would continually break down during use. This was supported by the fact that it was not possible to obtain reproducible results unless the forty minutes plating time was rigidly adhered to.

TABLE 6.6

<table>
<tr><th>Plating Time</th><th colspan="4"></th></tr>
<tr><td>50 minutes</td><td colspan="4">Chromium deposited, no microcracking, plastic container.</td></tr>
<tr><td>145 minutes</td><td colspan="4">Chromium deposited, no microcracking, plastic container</td></tr>
<tr><td>195 "</td><td colspan="4">Cell geometry changed, chromium deposited, no microcracking, plastic container.</td></tr>
<tr><td></td><td colspan="4">Solution transferred from a plastic to a glass container and left without plating for 30 minutes.</td></tr>
<tr><td></td><td colspan="4">Microcracking occurred when plating was continued.</td></tr>
<tr><td></td><td>$\bar{x}$</td><td>S.D.</td><td>No. of Results</td><td>Container</td></tr>
<tr><td>235 minutes</td><td>34</td><td>24.80</td><td>20</td><td>Glass</td></tr>
<tr><td></td><td colspan="4">Transfer solution to a plastic container</td></tr>
<tr><td>295 minutes</td><td>39</td><td>26.85</td><td>20</td><td>Plastic</td></tr>
</table>

TABLE 6.7

Catalyst	Amount added g/1	Calculated F g/1	Result
LiF	1.854	1.358	About 4 cracks on cathode
NaF	3.000	1.358	No cracking
KF	4.844	1.584	No cracking
CsF	5.647	0.706	About 4 cracks cathode
NH_4F	3.087	1.584	No cracking

Further tests were carried out to find the effect of solution ageing in glass and polythene containers and at the same time reduced chromium was estimated.

The results are set out in the following Tables 6.8 to 6.12.

Ten minutes before each of the plating times given the working cathodes were replaced with a freshly bright nickel plated one and replaced after ten minutes by the working cathode. Crack counts in all cases were done on the ten minute plated cathodes and taken horizontally twenty-five millimetres from the bottoms of the cathodes. The same chromium plating solution was used for each table of results, a new solution being made up for each new table.

TABLE 6.8

4.844 g/l potassium fluoride in a glass container, the same chromium plating solution being used throughout.

<table>
<tr><th>Estimated Cr^{+++} g/l</th><th>Plating time minutes</th><th>$\bar{x}$</th><th>S.D.</th><th>Number of results</th><th>Container</th></tr>
<tr><td>0.3</td><td>50</td><td>215</td><td>63.61</td><td>20</td><td>glass</td></tr>
<tr><td>1.0</td><td>160</td><td>226</td><td>46.91</td><td>20</td><td>glass</td></tr>
<tr><td>1.4</td><td>250</td><td>229</td><td>36.83</td><td>20</td><td>glass</td></tr>
<tr><td>2.0</td><td>370</td><td>196</td><td>42.04</td><td>20</td><td>glass</td></tr>
<tr><td>2.1</td><td>460</td><td>84</td><td>29.15</td><td>20</td><td>glass</td></tr>
<tr><td>2.2</td><td>550</td><td>91</td><td>29.95</td><td>20</td><td>glass</td></tr>
<tr><td colspan="6">Left without plating for 900 minutes then 1 g/l potassium fluoride added</td></tr>
<tr><td>2.3</td><td>595</td><td>466</td><td>55.46</td><td>20</td><td>glass</td></tr>
<tr><td>2.3</td><td>645</td><td>466</td><td>85.46</td><td>20</td><td>glass</td></tr>
</table>

Table 6.8 shows the decrease in crack counts $\bar{x}$ and the increase in reduced chromium Cr^{+++} with use of the solution. The crack count fell rapidly at 2.1 g/l reduced chromium and it could be inferred that this amount of reduced chromium caused the fall in crack counts. However, addition of more potassium fluoride increased the crack count

at the same concentration of reduced chromium indicating that the effect was not due to reduced chromium.

TABLE 6.9

4.844 g/l potassium fluoride in a glass/polythene container

Estimated Cr^{+++} g/l	Plating time minutes	$\bar{x}$	S.D.	Number of results	Container
0.3	50	215	63.61	20	glass
1.6	175	183	28.54	20	polythene
2.0	340	70	30.14	20	polythene
Left without plating in a plastic container for 1100 minutes					
2.4	430	35	31.12	20	polythene
2.6	540	35	22.34	20	polythene
	1 g/l potassium fluoride added				
2.6	590	599	68.66	20	polythene
	1 g/l potassium fluoride added				
2.9	640	No chromium deposition		-	polythene

The increase in reduced chromium with plating time was similar to the results of Table 6.8. Again the crack count dropped with solution age and the addition of a relatively small amount of potassium fluoride dramatically increased the crack count. This was interesting because plating was carried out in a polythene container and it was expected that addition of a simple fluoride would not cause an increase in cracking unless the fluoride had reacted with glass.

TABLE 6.10

2.0 g/l hydrofluosilicic acid in a glass container, the same chromium plating solution being used throughout

Plating time minutes	$\overline{x}$	S.D.	Number of results	Container
50	555	86.99	20	glass
200	553	72.16	20	glass
325	305	131.27	20	glass
Left without plating for 1020 minutes then 1 g/l hydrofluosilicic acid added.				
420	859	61.77	20	glass

Again a drop in crack counts was observed with use of the solution, addition of hydrofluosilicic acid increasing the microcracking.

TABLE 6.11

2.0 g/l hydrofluosilicic acid in a plastic container, the same chromium plating solution being used throughout

Plating time minutes	$\overline{x}$	S.D.	Number of results	Container
50	737	62.54	20	polythene
Left without plating for 1040 minutes				
260	508	89.98	20	polythene
455	431	68.27	20	polythene
560	328	93.30	20	polythene
Left without plating for a further 1040 minutes then 1 g/l hydrofluosilicic acid added				
610	1038	145.00	20	polythene

Again a drop in crack counts was observed with use of the solution addition of hydrofluosilicic acid increasing the crack count.

From a superficial examination of Tables 6.10 and 6.11 it appeared that catalyst breakdown did not occur as readily in polythene as in glass.

It was concluded that catalyst breakdown occurred in both plastic and glass containers and this will be discussed later.

In order to separate out the effects of reduced chromium and catalyst breakdown six solutions were made up each with 4.844 g/l potassium fluoride with reduced chromium introduced by oxalic acid additions. In each case chromium plating was done on a working cathode for forty minutes and then ten minutes on a freshly plated bright nickel plated one. Crack counts were taken on the ten minutes plated cathodes, taken horizontally twenty-five millimetres from the bottom.

TABLE 6.12

Effect of Reduced Chromium on Crack Count

Calculated Cr^{+++} g/l	Estimated Cr^{+++} g/l	$\bar{x}$	S.D.	Number of results
0.0	0.3	215	63.61	20
0.3	0.6	172	47.92	20
1.0	1.6	167	27.07	20
2.0	2.0	184	49.43	20
4.0	4.0	269	62.45	20
6.0	6.0	274	43.62	20

Reduced chromium had very little effect on crack count and reduction in crack count with use of solution was attributed to catalyst breakdown.

COMPARISON OF GLASS AND POLYTHENE CONTAINERS

A comparison was made of the same catalyst used under exactly similar conditions in glass and polythene containers. 2.0 g/l of hydrofluosilicic acid were added to two chromium plating solutions in glass and polythene containers and plating done on a working cathode in each case for forty minutes and then ten minutes on a freshly plated bright nickel plated one. Crack counts were taken on the ten minute plated cathode, horizontally twenty-five millimetres from the bottom.

The results were analysed by comparing the variances of the crack counts and the means then compared using students t-test.

			Number of results
Glass	$\bar{x} = 555$	$V = 7569.35$	20
Polythene	$\bar{x} = 737$	$V = 3912.85$	20

$$\text{F ratio} = \frac{7569.35}{3912.85} = 1.93$$

$$\phi_1 = \phi_2 = (20 - 1) = 19$$

Probability 5%-10%

The variances were just not significant and the means were then compared using the t-test.

$$\text{S.D. from both lots of data} = 75.76$$

$$\therefore \quad t = 7.621$$

$$\phi = (20 + 20 - 2) = 38$$

Probability 0.1%

Statistical evidence exists for a difference between the crack counts and since the lowest crack count was obtained using a glass container this suggests that catalyst breakdown was occurring more in glass than in polythene.

The numerical difference of (737 - 555) = 182 may well be experimental error and no firm conclusions can be drawn from this evidence.

COMPARISON OF CURRENT SUPPLY

Similarly the effects of current supply were investigated. Rectified A.C. and 12 volt battery supplies were compared using solutions containing 4.844 g/l potassium fluoride in glass containers.

	$\bar{x}$	Variance	Number of results
Battery	253	2472.82	20
Rectified A.C.	215	4046.97	20

$$\text{F ratio} = \frac{4046.97}{2472.82} = 1.64$$

$$\phi_1 = \phi_2 = (20 - 1) = 19$$

Probability over 10%

∴ Not significant

S.D. from both lots of data = 57.09

$t = 2.094$

$$\phi = (20 + 20 - 2) = 38$$

Probability less than 5%

Although the probability was statistically significant, the numerical difference being only (253 - 315) = 38 was considered to be well within experimental error.

The effects of current supply were also compared using solutions containing 2.0 g/l hydrofluosilicic acid in polythene containers with the following results.

	$\bar{x}$	Variance	Number of results
Battery	617	5339.18	20
Rectified A.C.	555	7569.35	20

$$\text{F ratio} = \frac{7569.35}{5339.18} = 1.42$$

$$\phi_1 = \phi_2 = (20 - 1) = 19$$

Probability over 10%

$\therefore$ Not significant

S.D. from both lots of data = 80.33

$t = 2.441$

$$\phi = (20 + 20 - 2) = 38$$

Probability less than 5%

This probability was statistically significant, the numerical difference being (617 - 555) = 62 was again considered to be well within experimental error.

Although statistical differences were found between the use of rectified A.C. current supply and a 12 volt battery supply they were considered to be well within experimental error. The numerical differences in crack counts of 38 cracks/10 mm and 62 cracks/10 mm respectively were therefore attributed to experimental error.

CHAPTER 7

ANALYSIS OF HULL CELL RESULTS

COVERING POWER IN HULL CELLS

Rousselot[57] defined Covering Power as the minimum current density at which the deposit will start to form. From an examination of the experimental results it appeared that the current densities at which chromium deposition commenced on the Hull Cell cathodes were related to the fluoride concentrations. Chessin and Seyb[58] also found that fluorides reduced chromium coverage. To investigate any possible relationships between Covering Power and fluoride concentration linear regression analysis was done on the experimental results. Current density in A/dm^2 at which chromium deposition commenced was taken as the dependent variable and the concentration of fluoride in g/l as the independent one. (Table 7.1 and Fig. 7.1 and 7.2)

TABLE 7.1

LINEAR REGRESSION ANALYSIS OF HULL CELL CATHODE RESULTS

	m	c	r	Ø	% Prob.	
LiF	8.60	−1.19	0.987	5	0.1	
NaF	8.75	−0.85	0.991	7	0.1	
KF	9.35	−1.56	0.985	7	0.1	
RbF	10.74	−1.46	0.985	1	10	
CsF	19.76	−2.78	0.993	3	0.1	
NH_4F	12.78	−1.84	0.965	6	0.1	
Li_2SiF_6	4.66	−0.56	0.992	5	0.1	
Na_2SiF_6	4.35	−0.55	0.983	2	2	
K_2SiF_6	2.96	3.01	0.991	2	1	some insolubles
Cs_2SiF_6	7.10	−1.06	0.999	2	0.1	
$(NH_4)_2SiF_6$	3.68	1.99	0.998	3	0.1	
H_2SiF_6	4.79	0.86	0.986	3	1	

With the exception of rubidium fluoride all the correlation coefficients were significant at the 2% level or less. Although rubidium fluoride was only significant at the 10% level the results had only one degree of freedom and it also followed the same pattern as the other fluorides. In view of this rubidium fluoride results were included for further analysis.

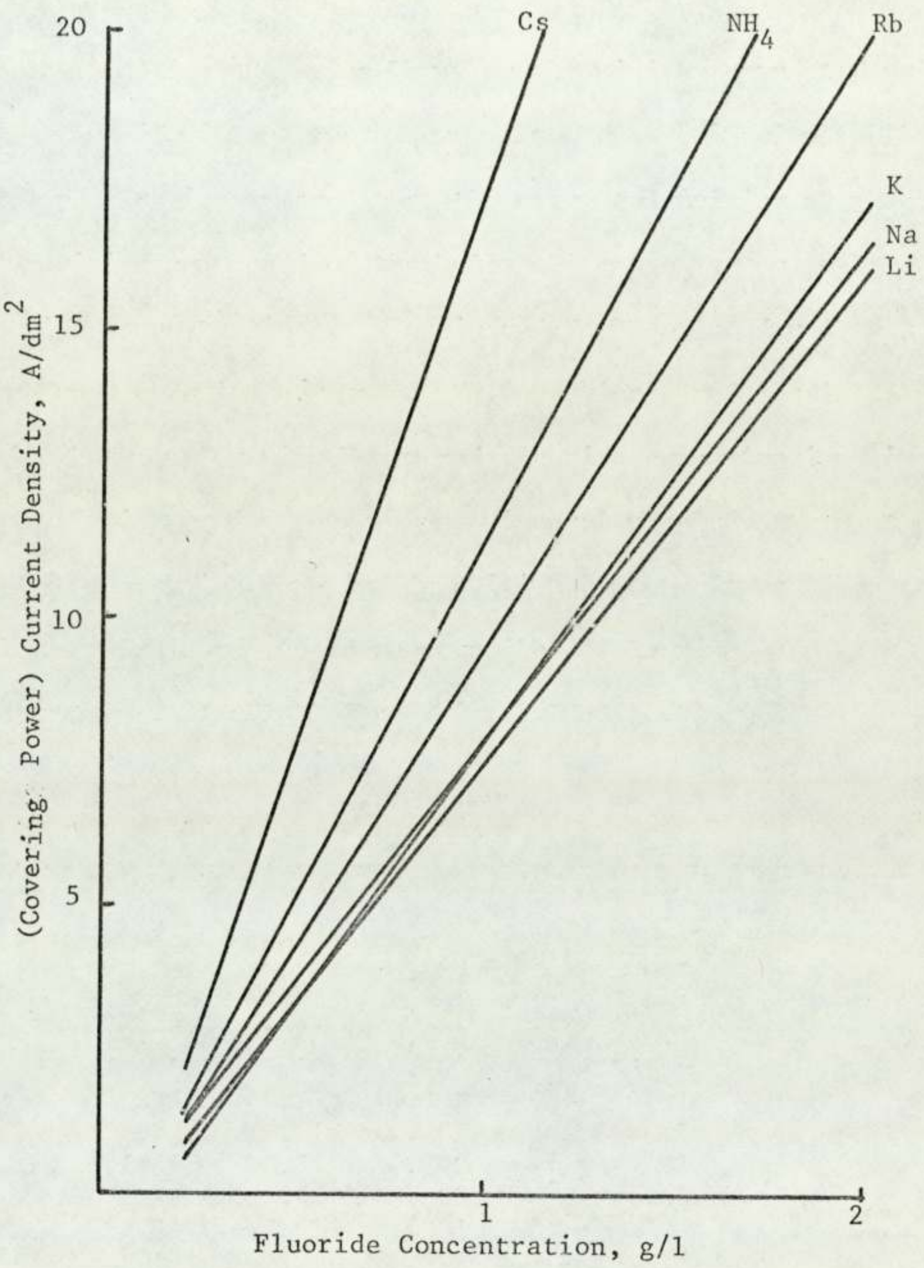

FIG. 7.1. Relationships between covering power and fluoride concentration for simple fluorides

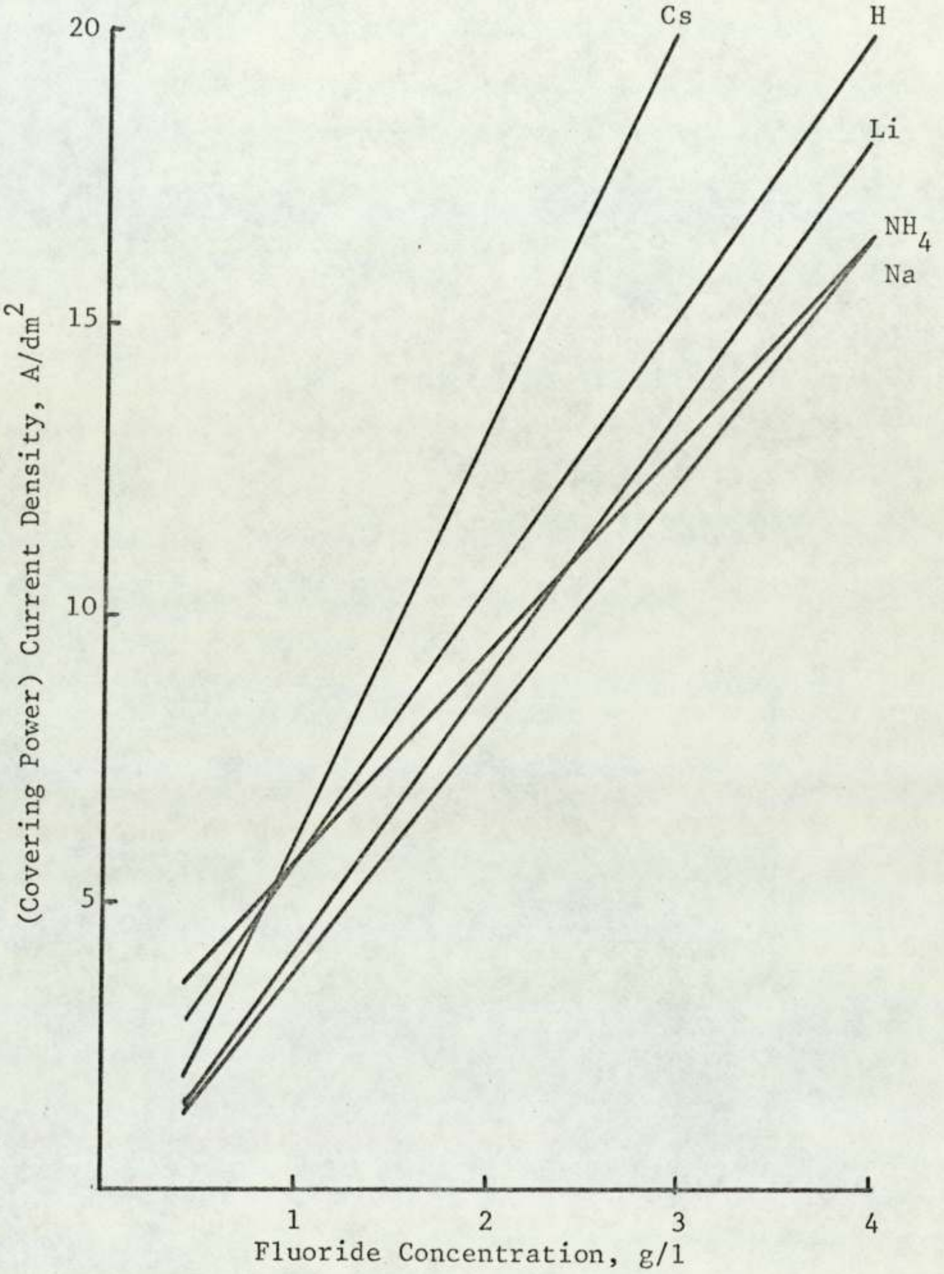

FIG. 7.2. Relationships Between Covering Power and Fluoride Concentration for Complex Fluorides

The fluorides inhibited the deposition of chromium at the lower current densities, the amount of inhibition increasing with fluoride concentration. The slopes of the curves increasing from 8.60 for lithium fluoride to 19.76 for caesium fluoride showed the influence of the alkali metal part of the molecule on covering power.

These results were divided into two groups: the simple fluorides of lithium, sodium, potassium, rubidium and caesium in one group and the complex fluorides of lithium, sodium and caesium in a second group. Ammonium compounds were not included because ammonium, NH_4 cannot be placed in the same vertical column of the periodic table as the alkali metals. The fluorosilicates of hydrogen and potassium were not included because their results did not follow the general pattern, also potassium fluorosilicate was not completely soluble in the chromium plating solutions at the higher fluoride concentrations. It was considered that further analysis of the complex fluoride results would be unreliable in view of the small number of degrees of freedom available, although such an analysis was done for the sake of completeness.

Linear regression analysis was done on the data for each of the two groups. The slopes m, i.e. a measure of the rate of change of covering power with fluoride concentration, were taken as the dependent variables with a blanket coverage of various parameters of the alkali metals taken in turn as the independent variables. (Table 7.2 and Fig. 7.3.)

No correlation was found between results of the complex fluorides and various parameters of the alkali metals as was expected. With the simple fluorides linear relationships were found between m and atomic number and also between m and atomic weight; the correlation coefficients being significant at the 5% level. Visual examination of the slopes, m, in Table 7.1. showed that caesium fluoride was much more

TABLE 7.2

REGRESSION ANALYSIS OF HULL CELL DERIVED RESULTS

Independent Variable	Type of Fluoride	Correlation Coefficient	Probability %
Atomic number	Simple	0.892	5
Atomic number	Simple without Cs	0.983	2
Atomic weight	Simple	0.907	5
Atomic weight	Simple without Cs	0.991	1
Ionic radius	Simple	0.742	below 10
Ionic radius	Simple without Cs	0.900	just 10
Atomic radius	Simple	0.725	below 10
Atomic radius	Simple without Cs	0.860	below 10
Ionisation potential	Simple	-0.718	below 10
Ionisation potential	Simple without Cs	-0.868	below 10
Cube edge	Simple	0.720	below 10
Cube edge	Simple without Cs	0.873	below 10
Melting point	Simple	-0.608	below 10
Melting point	Simple without Cs	-0.801	below 10
Boiling point	Simple	-0.496	below 10
Boiling point	Simple without Cs	-0.689	below 10
Atomic number	Complex	0.969	below 10
Atomic weight	Complex	0.995	below 10
Ionic radius	Complex	0.947	below 10
Atomic radius	Complex	0.919	below 10
Ionisation potential	Complex	-0.966	below 10
Cube edge	Complex	0.915	below 10
Melting point	Complex	-0.779	below 10
Boiling point	Complex	-0.644	below 10

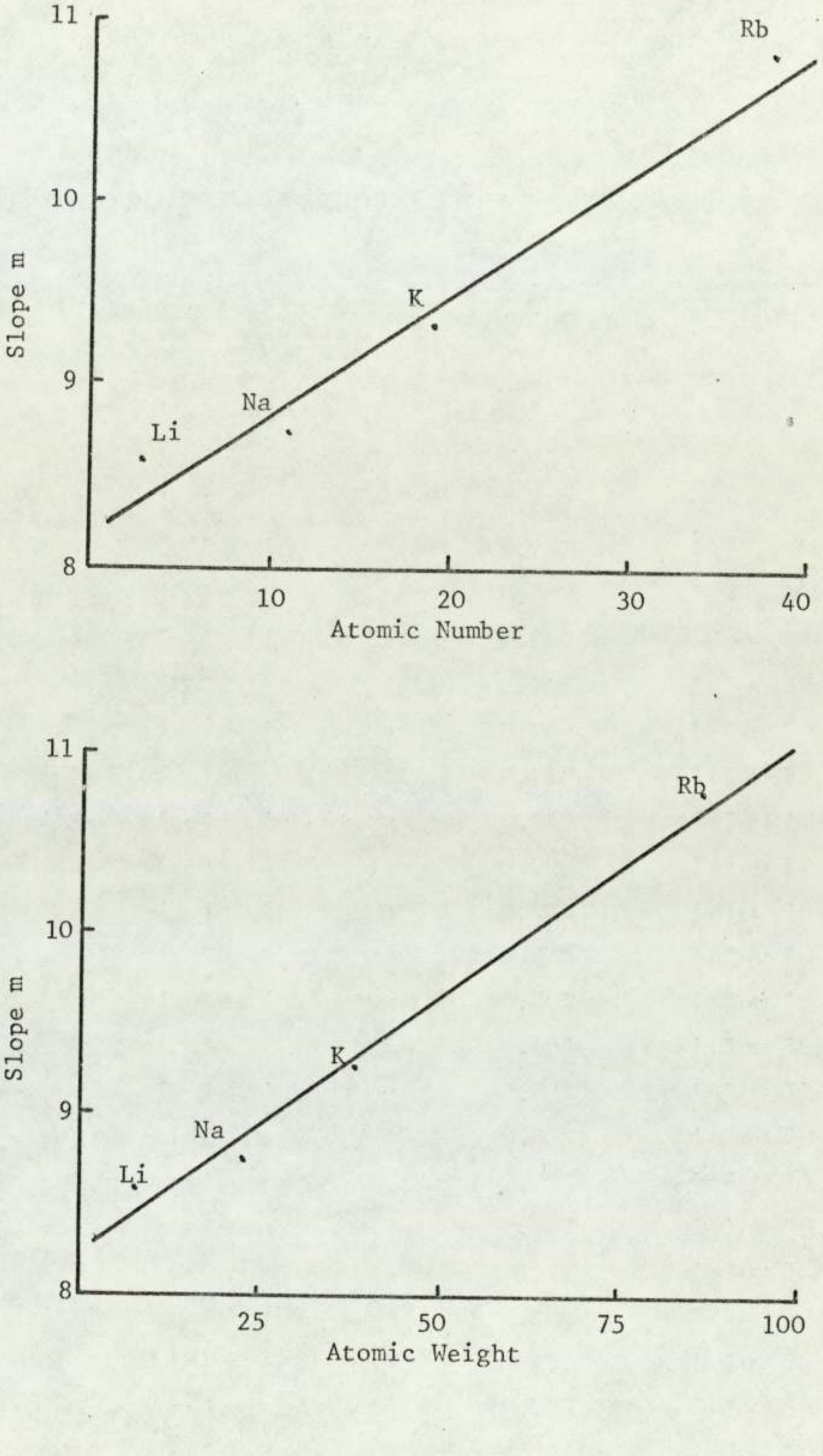

FIG. 7.3. Regression Analysis of Covering Power Results for Simple Fluorides

effective than the other fluorides. The calculations were therefore repeated for the simple fluorides but with the omission of the caesium fluoride results. In all cases an improvement was made in the correlation coefficients although no more linear relationships became statistically significant at the 5% level.

This was taken as further evidence, although in this case somewhat limited, of the apparently anomalous behaviour of caesium.

Since relationships exist for simple fluorides between m, a measure of the rate of change of covering power with fluoride concentration and atomic number and also m and atomic weight it is considered that the alkali metal influences covering power.

STATISTICAL ANALYSIS OF MICROCRACKING ON HULL CELL CATHODES

Crack counts were carried out on Hull Cell cathodes along a line 25 millimetres from and parallel to the bottom of the cathode. Counts were taken every millimetre beginning at the high current density end and continued until cracking ceased. The current density at one millimetre intervals along the Hull Cell cathode was calculated from:

$$i = I(5.1 - 5.24 \log_{10} X)$$

where i = current density in A/dm^2

I = total current in amps, in this case 5

X = distance from high current density end of cathode per 10 millimetres

Alternative formulae[8,62] have been proposed giving slightly lower current density values at the high current density end and slightly higher values at the low current density end.

To investigate any possible relationships between cracks/10 mm as the dependent variable and current density in A/dm^2 together with fluoride concentration in g/l as the independent variables, multiple regression analysis was carried out on the experimental results.

DISCUSSION OF MULTIPLE REGRESSION ANALYSIS METHODS

This is the dependence of the dependent variable Y on at least two other independent variables X, Z, etc. With only one independent variable the results may be plotted graphically in one plane but this is not possible for two independent variables. When Y depends partly on X and partly on Z for its value solid geometry is required, any observation involving three numbers Y, X and Z. X and Z can be represented by a point on graph paper and the values of Y corresponding to this point are on a vertical axis perpendicular to the graph paper. The surface determined by this method is the regression surface and is a plane for multiple linear regression, in the case of multiple curvilinear regression the surface is curved.

For linear multiple regression the data may be represented by

$$Y = a + b_1X + b_2Y$$

and for curvilinear multiple regression by

$$Y = a + b_1X^2 + b_2Y^2$$

where a, b_1, b_2 are constants, being different for the two equations. Many variations of these equations are possible and they will not be discussed here.

The methods of calculating these equations from the experimental data were similar to the Method of Least Squares for linear regression with only one independent variable but because of the complexity of the calculations involved it was necessary to use an ICL 1905 Computer. The computer facilities included a statistical analysis publication[89] the use of which greatly simplified programme writing. The data was presented on punched cards and these data cards were surrounded by control cards for presentation to the computer. The output which included various statistical tests was by lineprinter.

All the printed output was not used and information is only given on the statistical tests used in this analysis to find the goodness of fit of the calculated regression equations to the experimental results.

MULTIPLE CORRELATION COEFFICIENT R

This measures the overall extent of association between values of the dependent variables and the corresponding values of the independent variables and is given by

$$R^2 = \frac{\text{Sum of squares due to multiple regression}}{\text{Total sum of squares of y values about their mean}}$$

R^2 is also given by

$$R^2 = 1 - \frac{\text{error sum of squares}}{\sigma^2_y \times (n - 1)}$$

where σ^2_y = variance of y

n = number of observations

A value of zero for R gives no correlation and a value of one means that all the sample points lie exactly on the regression plane. The significance of R may be tested by reference to tables and entering at the correct number of degrees of freedom and total number of variables.

ERROR SUM OF SQUARES

This is the error sum of squares about the regression, that is the total amount of error unexplained by the regression. It is the sum of squares of the estimates of error in using the regression equation for prediction purposes, that is the sums of squares of the differences between experimental crack count and that calculated from the regression equation.

RESIDUAL ERROR (STANDARD ERROR)

This is the standard error of an estimate of the dependent variable using the regression equation and is given by

$$\left(\frac{\text{error sum of squares}}{n}\right)^{\frac{1}{2}}$$

For large sample sizes the confidence interval for the predicted dependent variable is given by the residual error multiplied by the appropriate value of t for the number of degrees of freedom of the regression equation and the required confidence level. That is the confidence interval for the predicted Y, $\hat{y}$ using the regression equation is given by

$$Y = \hat{y} \pm \text{residual error of } y \times t_{\phi}$$

where t_{ϕ} is the appropriate value for ϕ degrees of freedom. In about 95% of cases the actual values will be between two standard errors of the estimated values given by the regression equation.

TOTAL SUM OF SQUARES

This is the total variation which is the product of the variance for the dependent variable and the number of observations minus one.

RESIDUALS

Residuals are the differences between the observations and their value when calculated from the regression equation. These residuals should sum to zero but in practice do not quite do so because of rounding off error.

Examination of residuals may be done in several ways:

(1) Look for the largest residuals in size either positive or negative and should a few be much larger than others then these should be examined more closely. Possible causes may either be faulty experimentation or the effect may be genuine, the regression equation not being an exact fit to all the experimental results. Whatever the cause care must be taken before rejecting any observation on the basis of interval statistical evidence alone.

(2) Evidence of patterns in the residuals such as a general trend to either increase or decrease in both a positive and negative sense. Here again this may be either due to faulty experimentation or the regression equation not exactly fitting the experimental data.

(3) Splitting the residuals into three numerically equal groups, calculating the means and variances of each group and then testing for differences between the groups by the variance ratio F test.

(4) Plotting a graph of results calculated using the regression equation against the experimental results and including on the graph the confidence limits.

Other multiple regression analysis methods will be discussed as the occasion arises.

DETAILS OF COMPUTER PRINT OUT

Considerable variations were possible in the use of the regression analysis computer programme and it is impossible to discuss all the variations in a reasonable number of words. The variations most used included the facility of performing many operations on the data in one run and the use of alternative dependent and independent variables for one lot of experimental results.

The main information given in the print out is as below although all of it was not used.

REGRESSION

The name of the dependent variable was given together with the number of degrees of freedom. This was followed by the percentage level of significance of the independent variables together with the names of the independent variables in the regression set.

For each of the independent variables in turn the following were printed:

(a) The variable name.

(b) The regression coefficient.

(c) The standard error of the regression coefficient.

(d) The confidence error of the regression coefficient, that is the range up and down from the estimate of the regression coefficient within which the true regression coefficient can be expected to lie with the significance level specified. This is only calculated if the significance level is less than 99.00%.

(e) The value of t for the regression coefficient, that is the ratio of the regression coefficient to its standard error.

(f) The partial coefficient of the variable, which was not used.

(g) The multiple correlation coefficient.

(h) The error sum of squares of the variables.

(g) and (h) are those values that would occur if this variable were eliminated from the regression set.

VARIABLES NOT IN THE REGRESSION SET

(a) The variable name.

(b) The value of t, which is the value of t for the variable if that variable alone were added to the set.

(c) Partial correlation coefficient, which was not used.

(d) Multiple correlation coefficient.

(e) Error sum of squares.

(d) and (e) are those values that would occur if this variable were added to the regression set.

OTHER STATISTICAL OUTPUT

(a) The error sum of squares of the model.

(b) The residual error.

(c) The multiple correlation coefficient.

(d) The intercept term.

The intercept term together with the regression coefficient specifies the required equation.

DATA ANALYSIS

Multiple regression analysis was used for two main purposes.

(1) The investigation of the dependence of microcracking on variables such as current density and fluoride concentration.

(2) The construction of regression equations to give the best prediction of crack counts from other information such as current density and fluoride concentration.

The first reason is perhaps the more important one for the investigation of deposition mechanisms, the second one may be useful for commercial application in some instances.

PRELIMINARY DATA ANALYSIS

The data was kept in separate lots for each fluoride used, there being twelve lots of data, one for each of lithium, sodium, potassium, rubidium, caesium and ammonium fluorides; and lithium, sodium, potassium, caesium and ammonium fluorosilicates; and hydrofluosilicic acid. One each data card was punched the crack count, the current density at the point where the crack count was taken and also the concentration of fluoride for that particular Hull Cell cathode. Other information that may be of use in later calculations was also punched on the same card, this being atomic number, atomic weight, atomic radius and ionic radius of the alkali metals. Altogether about 900 data cards were used split unequally into twelve lots.

PRELIMINARY STATISTICAL ANALYSIS

To obtain information of any probable relationships between the dependent variable cracks and the independent variables current density and fluoride concentration, trial computer runs were made with lithium fluoride and lithium fluorosilicate data.

It was thought that the spaces between the cracks may be of more significance than the cracks themselves and therefore the transformation $\frac{1}{\text{cracks}}$ was used as an alternative dependent variable. The squares of concentration and current density were also introduced and models of the following form calculated.

$$\text{CRACKS} = k(\text{CURDEN}) + k_1(\text{CONCEN}) + k_2(\text{CURDN2}) + k_3(\text{CONCN2}) + k_4$$

$$\text{SPACES} = k(\text{CURDEN}) + k_1(\text{CONCEN}) + k_2(\text{CURDN2}) + k_3(\text{CONCN2}) + k_4$$

where CRACKS = cracks/10 mm

SPACES = $\frac{1}{\text{cracks}}$

CURDEN = current density in A/dm^2

CONCEN = concentration in g/l fluorine

CURDN2 = (CURDEN)^2

CONCN2 = (CONCEN)^2

k, k_1, k_2 ... = constants being numerically different for each equation.

Square terms were used because in chemical systems it is to be expected that reaction rates are proportional to some power of the concentration[90] and the same could be said to apply to current density.

To obtain information of the significance of the variables computer runs were done with the independent variables at significant level 9.00% and using the iterative procedure to build up models beginning with the most statistically significant independent variables.

Lithium fluoride with the dependent variable as cracks/10 mm showed the square of the fluoride concentration as the most significant independent variable with a t value of 7.84 for 44 degrees of freedom, significant at the 0.1% level. With the dependent variable as the reciprocal of cracks/10 mm the square of the fluoride concentration was again shown as the most significant independent variable with a t value of 6.14, significant at the 0.1% level. The following "best" model was built up with all terms having t values at the 2.5% level at least.

$$\text{SPACES} = k(\text{CURDEN}) + k_1(\text{CONCEN}) + k_2(\text{CURDN2}) + k_3$$

Lithium fluorosilicate with the dependent variable cracks/10 mm showed fluoride concentration as the most significant independent variable with a t value of 7.82 for 136 degrees of freedom significant at the 0.1% level. The following "best" model was built up with all terms having t values at the 0.1% level.

$$\text{CRACKS} = k(\text{CONCEN}) + k_1(\text{CONCN2}) + k_2$$

With the dependent variable as the reciprocal of cracks/10 mm fluoride concentration was again the most significant independent variable with a t value of 6.32 significant at the 0.1% level. The best model with t values all at the 0.1% level was

$$\text{SPACES} = k(\text{CURDEN}) + k_1(\text{CONCEN}) + k_2(\text{CONCN2}) + k_3$$

From this preliminary analysis of only two lots of data it was concluded that quantitative relationships existed between crack counts/ 10 mm as the dependent variable and fluoride concentration together with current density as the independent variables. Fluoride concentration probably had the most effect on crack counts and some transformation of cracks/10 mm may give a better fit of the experimental results to the regression equation.

It should be pointed out that the values of the t statistics calculated under preliminary statistical analysis are different from those calculated under detailed statistical analysis. This is because the preliminary t values have been calculated for the "best" models by an iterative procedure and these "best" models were not the same as those used under the detailed analysis.

DETAILED STATISTICAL ANALYSIS

The remainder of the data was analysed with the independent variables at a significance level of 99.00% because of the high values of t obtained in the preliminary analysis. This had the effect of putting all the independent variables into the regression equation without any significance test. Each of the twelve lots of data was run through the computer in turn and the goodness of fit of the data to each of the following models obtained.

$$\text{CRACKS} = k(\text{CURDEN}) + k_1(\text{CONCEN}) + k_2 \qquad \text{A}$$

$$\text{SPACES} = k(\text{CURDEN}) + k_1(\text{CONCEN}) + k_2 \qquad \text{B}$$

$$\text{CRACKS} = k(\text{CURDEN}) + k_1(\text{CONCEN}) + k_2(\text{CURDN2}) + k_3(\text{CONCN2}) + k_4 \qquad \text{C}$$

$$\text{SPACES} = k(\text{CURDEN}) + k_1(\text{CONCEN}) + k_2(\text{CURDN2}) + k_3(\text{CONCN2}) + k_4 \qquad \text{D}$$

The rubidium fluoride results were considered unreliable because of lack of experimental data and are therefore not considered further.

With the dependent variable cracks/10 mm and current density with fluoride concentration as independent variables, fluoride concentration had t values significant at the 1% level at least, with the single exception of ammonium fluoride whose t value was not significant at all. The variable, current density was only significant above the 5% level in the cases of caesium fluoride, caesium fluorosilicate and ammonium fluoride.

With the dependent variable cracks/10 mm and current density, fluoride concentration together with their squares as independent variables the results were not as clear cut. A possible explanation is that the current density effect is distributed between the variables current density and (current density)^2 and similarly fluoride concentration between the variables fluoride concentration and (fluoride concentration)^2. In the case of lithium fluoride the t statistic for fluoride concentration dropped from 7.66 to 0.24 with the introduction of the square terms. Nevertheless with the exceptions of lithium fluoride, caesium fluoride and ammonium fluoride one of the current density variables and one of the fluoride concentration variables were significant at the 5% level at least.

TABLE 7.3

DEPENDENT VARIABLE CRACKS

LITHIUM FLUORIDE (NUMBER OF POINTS 46)

	Regression Coefficient	t statistic	Regression Coefficient	t statistic
current density	2.6	1.94	10.6	0.99
fluoride concentration	171.4	7.66	32.4	0.24
(current density)^2	-	-	-0.1	0.83
(fluoride concentration)^2	-	-	53.6	1.01

LITHIUM FLUOROSILICATE (138)

	Regression coefficient	t statistic	Regression Coefficient	t statistic
current density	-0.1	0.05	54.5	5.22
fluoride concentration	244.1	7.77	1088.7	7.56
(current density)^2	-	-	-0.9	5.14
(fluoride concentration)^2	-	-	-216.1	6.09

SODIUM FLUORIDE (87)

	Regression Coefficient	t statistic	Regression Coefficient	t statistic
current density	0.007	0.01	-9.9	3.11
fluoride concentration	114.7	6.93	-185.3	2.48
(current density)^2	-	-	0.1	2.95
(fluoride concentration)^2	-	-	132.9	4.07

SODIUM FLUOROSILICATE (71)

	Regression Coefficient	t statistic	Regression Coefficient	t statistic
current density	-3.2	1.07	38.0	2.44
fluoride concentration	310.5	11.24	-348.0	1.79
(current density)^2	-	-	-0.6	2.60
(fluoride concentration)^2	-	-	161.9	3.38

POTASSIUM FLUORIDE (77)

	Regression Coefficient	t statistic	Regression Coefficient	t statistic
current density	0.3	0.53	-7.7	3.12
fluoride concentration	103.9	7.62	-213.6	3.99
(current density)^2	-	-	0.1	3.02
(fluoride concentration)^2	-	-	138.5	5.98

POTASSIUM FLUOROSILICATE (84)

	Regression Coefficient	t statistic	Regression Coefficient	t statistic
current density	0.8	0.30	44.5	4.26
fluoride concentration	94.8	6.90	421.0	10.08
(current density)^2	-	-	-0.7	4.31
(fluoride concentration)^2	-	-	-47.0	8.34

RUBIDIUM FLUORIDE (33)

	Regression Coefficient	t statistic	Regression Coefficient	t statistic
current density	2.8	5.35	0.7	0.19
fluoride concentration	58.0	4.16	-	-
(current density)^2	-	-	0.03	0.64
(fluoride concentration)^2	-	-	32.7	3.79

CAESIUM FLUORIDE (52)

	Regression Coefficient	t statistic	Regression Coefficient	t statistic
current density	1.3	2.81	1.3	0.05
fluoride concentration	65.3	3.21	225.2	2.21
(current density)^2	-	-	0.005	0.14
(fluoride concentration)^2	-	-	-123.2	1.60

CAESIUM FLUOROSILICATE (54)

	Regression Coefficient	t statistic	Regression Coefficient	t statistic
current density	9.3	2.23	115.9	5.27
fluoride concentration	498.0	6.94	2238.2	5.24
(current density)^2	-	-	-1.6	4.84
(fluoride concentration)^2	-	-	-613.9	4.11

AMMONIUM FLUORIDE (66)

	Regression Coefficient	t statistic	Regression Coefficient	t statistic
current density	0.5	2.31	1.6	1.03
fluoride concentration	4.2	0.72	104.9	4.02
(current density)^2	-	-	-0.009	0.42
(fluoride concentration)^2	-	-	-46.2	3.94

AMMONIUM FLUOROSILICATE (97)

	Regression Coefficient	t statistic	Regression Coefficient	t statistic
current density	3.6	1.33	54.7	6.03
fluoride concentration	145.5	5.81	731.2	13.10
(current density)^2	-	-	-0.8	5.36
(fluoride concentration)^2	-	-	-123.3	11.16

HYDROFLUOSILICIC ACID (89)

	Regression Coefficient	t statistic	Regression Coefficient	t statistic
current density	3.2	1.81	49.9	5.34
fluoride concentration	245.4	12.51	579.3	7.99
(current density)^2	-	-	-0.7	4.86
(fluoride concentration)^2	-	-	-102.8	4.71

DEPENDENT VARIABLE SPACES

LITHIUM FLUORIDE (46)

	Regression Coefficient	t statistic	Regression Coefficient	t statistic
current density	-0.00091	5.61	-0.00419	3.41
fluoride concentration	-0.02173	7.97	-0.03492	2.25
(current density)^2	-	-	0.00004	2.69
(fluoride concentration)^2	-	-	0.00580	0.95

LITHIUM FLUOROSILICATE (138)

	Regression Coefficient	t statistic	Regression Coefficient	t statistic
current density	-0.00015	1.84	-0.00092	2.42
fluoride concentration	-0.00689	6.19	-0.04181	7.98
(current density)^2	-	-	0.00001	1.86
(fluoride concentration)^2	-	-	0.00880	6.81

SODIUM FLUORIDE (87)

	Regression Coefficient	t statistic	Regression Coefficient	t statistic
current density	-0.00032	3.03	0.00084	1.50
fluoride concentration	-0.02924	10.93	-0.00454	0.35
(current density)^2	-	-	-0.00002	2.02
(fluoride concentration)^2	-	-	-0.01089	1.90

SODIUM FLUOROSILICATE (71)

	Regression Coefficient	t statistic	Regression Coefficient	t statistic
current density	-0.00042	3.71	-0.00056	0.91
fluoride concentration	-0.1219	11.61	-0.03492	4.56
(current density)^2	-	-	0.00001	0.32
(fluoride concentration)^2	-	-	0.00567	3.01

POTASSIUM FLUORIDE (77)

	Regression Coefficient	t statistic	Regression Coefficient	t statistic
current density	-0.00057	4.31	0.00054	0.80
fluoride concentration	-0.02928	8.91	0.02665	1.81
(current density)^2	-	-	-0.00002	1.49
(fluoride concentration)^2	-	-	-0.02448	3.85

POTASSIUM FLUOROSILICATE (84)

	Regression Coefficient	t statistic	Regression Coefficient	t statistic
current density	-0.00010	0.76	-0.00040	0.71
fluoride concentration	-0.00353	5.31	-0.01973	8.67
(current density)^2	-	-	0.00001	0.60
(fluoride concentration)^2	-	-	0.00227	7.39

RUBIDIUM FLUORIDE (33)

	Regression Coefficient	t statistic	Regression Coefficient	t statistic
current density	-0.00010	4.55	-0.00231	1.84
fluoride concentration	-0.02218	4.29	-	-
(current density)^2	-	-	0.00002	1.14
(fluoride concentration)^2	-	-	-0.01403	4.46

CAESIUM FLUORIDE (52)

	Regression Coefficient	t statistic	Regression Coefficient	t statistic
current density	-0.00049	3.45	-0.00109	1.44
fluoride concentration	-0.02625	4.30	-0.10258	3.49
(current density)^2	-	-	0.00001	0.62
(fluoride concentration)^2	-	-	0.05869	2.65

CAESIUM FLUOROSILICATE (54)

	Regression Coefficient	t statistic	Regression Coefficient	t statistic
current density	-0.00021	1.62	-0.00082	1.25
fluoride concentration	-0.02606	11.68	-0.10709	8.35
(current density)^2	-	-	0.00001	0.81
(fluoride concentration)^2	-	-	0.02858	6.37

AMMONIUM FLUORIDE (66)

	Regression Coefficient	t statistic	Regression Coefficient	t statistic
current density	-0.00029	1.94	-0.00154	1.56
fluoride concentration	-0.00345	0.92	-0.06811	4.40
(current density)^2	-	-	0.00001	1.02
(fluoride concentration)^2	-	-	0.02965	3.92

AMMONIUM FLUOROSILICATE (97)

	Regression Coefficient	t statistic	Regression Coefficient	t statistic
current density	0.00294	0.50	0.03773	1.19
fluoride concentration	-0.06958	1.29	-0.26960	1.38
(current density)^2	-	-	-0.00057	1.15
(fluoride concentration)^2	-	-	0.03941	1.02

HYDROFLUOSILICIC ACID (89)

	Regression Coefficient	t statistic	Regression Coefficient	t statistic
current density	-0.00010	0.91	-0.00154	2.59
fluoride concentration	-0.01343	10.85	-0.04030	8.75
(current density)^2	-	-	0.00002	2.14
(fluoride concentration)^2	-	-	0.00829	5.99

With the dependent variable as the reciprocal of cracks/10 mm and current density with fluoride concentration as independent variables, fluoride concentration had t values significant at the 0.1% level with the exceptions of ammonium fluoride and ammonium fluorosilicate whose t values were not significant. The variable current density was significant at the 1% level, with the exceptions of lithium fluorosilicate, potassium fluorosilicate, caesium fluorosilicate, ammonium fluoride, ammonium fluorosilicate and hydrofluosilicic acid which were all not significant at the 5% level.

With the dependent variable as the reciprocal of cracks/10 mm and the inclusion of all four independent variables the results were again not as clear cut and for the same reasons. One of the current density variables and one of the fluoride concentration variables was significant at the 5% level at least in the cases of lithium fluoride, lithium fluorosilicate and hydrofluosilicic acid. One of the concentration terms was significant at the 5% level at least, in all cases with the two exceptions of sodium fluoride and ammonium fluorosilicate. One of the current density variables was significant at the 5% level only in the cases of lithium fluoride, lithium fluorosilicate, sodium fluoride, ammonium fluorosilicate and hydrofluosilicic acid.

From this analysis of the complete data considerable evidence is available showing that fluoride concentration has a much more important effect on crack count than current density, over the range of current densities used. This is seen to be particularly so when the statistics for the equations with only two independent variables are examined.

EXAMINATION OF MULTIPLE CORRELATION COEFFICIENTS

To obtain evidence of the goodness of fit of the experimental points to the calculated regression equations based on models A, B, C, D, page 116, an examination was made of the multiple correlation coefficients, Table 7.4.

TABLE 7.4

	DEPENDENT VARIABLE CRACKS/10mm		DEPENDENT VARIABLE RECIPROCAL OF CRACKS/10 mm	
	2 independent variables	4 independent variables	2 independent variables	4 independent variables
LiF	0.764	0.779	0.820	0.850
Li_2SiF_6	0.557	0.720	0.496	0.667
NaF	0.617	0.714	0.766	0.786
N_2SiF_6	0.806	0.847	0.836	0.859
KF	0.676	0.811	0.724	0.782
K_2SiF_6	0.630	0.849	0.544	0.766
CsF	0.526	0.565	0.624	0.684
Cs_2SiF_6	0.715	0.845	0.856	0.924
NH_4F	0.284 not significant	0.416	0.252 not significant	0.504
$(NH_4)_2SiF_6$	0.574	0.868	0.132 not significant	0.203 not significant
H_2SiF_6	0.812	0.876	0.766	0.844

With the exception of some of the ammonium salts all the coefficients were significant at the 1% level at least. For ammonium fluoride the 1% level was reached when all four independent variables were introduced. The coefficients for ammonium fluorosilicate with the dependent variable reciprocal of cracks/10 mm never became significant with either two or four independent variables.

The overall general pattern of Table 7.4 shows that the introduction of four independent variables gives a higher multiple correlation coefficient in all cases.

FURTHER STATISTICAL ANALYSIS

Further analysis was considered desirable for the following reasons.

(1) To find the best transformation of crack counts/10 mm.

(2) To find the best number and form of independent variables.

(3) To combine all the data in one regression equation if possible.

Since cracks/10 mm and its reciprocal gave quantitative relationships similar transformations were investigated, the following being used in turn for the dependent variable.

$\text{CRACKS} = \text{cracks/10 mm}$

$\text{SPACES} = \dfrac{1}{\text{cracks}} = \text{reciprocal of cracks/10 mm}$

$\text{CRACK2} = (\text{CRACKS}) \times (\text{CRACKS}) = \text{the square of cracks/10mm}$

$\text{LGCRAK} = \text{ALOG10(CRACKS)} = \log_{10} \text{cracks/10 mm.}$

The experimental results were processed by the computer to find the goodness of fit to the following models.

$$\text{CRACKS} = k(\text{CURDEN}) + k_1(\text{CONCEN}) + k_2 \qquad \text{E}$$

$$\text{CRACKS} = k(\text{CURDEN})+k_1(\text{CONCEN})+k_2(\text{CURDN2})+k_3(\text{CONCN2})+k_4(\text{CURCON})+k_5 \qquad \text{F}$$

In both equations CRACKS were replaced in turn by SPACES, CRACK2 and LGCRAK where

CURDEN = current density in A/dm^2
CONCEN = concentration in g/l fluorine
CURDN2 = $(\text{CURDEN})^2$
CONCN2 = $(\text{CONCEN})^2$
CURCON = (CURDEN) x (CONCEN)

the term CURCON was introduced for symmetry reasons.

Although some of these models had been calculated previously they were recalculated for ease of comparison.

The experimental results for lithium fluoride and lithium fluorosilicate were processed to find the goodness of fit of the data to the above models, E and F, page 126.

The multiple correlation coefficients are listed in Table 7.5.

TABLE 7.5

DEPENDENT VARIABLE	2 INDEPENDENT VARIABLES		5 INDEPENDENT VARIABLES	
	LiF	Li_2SiF_6	LiF	Li_2SiF_6
cracks/10 mm	0.764	0.557	0.808	0.721
reciprocal of cracks/10 mm	0.820	0.496	0.912	0.678
the square of cracks/10 mm	0.632	0.475	0.678	0.631
$\log_{10}$ cracks/10 mm	0.854	0.591	0.909	0.766

All the coefficients were significant at the 1% level at least and an increase in the number of independent variables from two to give gave higher correlation coefficients. The introduction of a fifth independent variable, the symmetry term CURCON, gave improvements over four independent variables. Comparing the results of Table 7.4 with Table 7.5, in the case of lithium fluoride the coefficient increased from 0.779 to 0.808 for cracks/10 mm and from 0.850 to 0.912 for the reciprocal of cracks/10 mm. The improvement for lithium fluorosilicate was not so great being from 0.720 to 0.721 for cracks/10 mm and from 0.667 to 0.678 for the reciprocal of cracks/10 mm.

ANALYSIS OF VARIANCE OF REGRESSION EQUATION VARIABLES FOR LiF AND Li_2SiF_6

To obtain further evidence for using a model with either two or five independent variables an analysis of variance was carried out on the regression equations for lithium fluoride and lithium fluorosilicate. Full details of the method are given in the case of lithium fluoride for the dependent variable cracks/10 mm followed by analysis of variance tables only for the remainder of the dependent variables for both cracks/10 mm and its reciprocal.

METHOD FOR ANALYSIS OF VARIANCE

LITHIUM FLUORIDE, DEPENDENT VARIABLE CRACKS/10 mm

Obtain the standard deviation from the computer print out for the appropriate regression equation with two independent variables and the dependent variable cracks/10 mm.

$$
\begin{aligned}
\text{Standard deviation} &= 131.164 \\
\therefore\ \text{Variance} &= (131.164)^2 \\
\therefore\ \text{Total sum of squares} &= (131.164)^2 \text{ x degrees of freedom} \\
&= (131.164)^2 \text{ x } (46 - 1) \\
&= 774180 = (e)
\end{aligned}
$$

A check on the total sum of squares may be obtained from the multiple correlation coefficient R, where

$$R^2 = 1 - \frac{\text{error sum of squares}}{{}^{2}{}_{y} \text{ x } (n - 1)}$$

$$\sigma^2_y \text{ x } (n - 1) = \text{total sum of squares}$$

$$\therefore \; R^2 = 1 - \frac{\text{error sum of squares}}{\text{total sum of squares}}$$

$$\text{total sum of squares} = \frac{\text{error sum of squares}}{1 - R^2}$$

The appropriate values of R and error sum of squares may be obtained from the computer print out

$$\therefore \; \text{total sum of squares} = \frac{322096}{1 - (0.764)^2}$$

$$= \underline{773703} = (e)$$

The two methods used for calculating total sum of squares would not be expected to give exactly the same result because of rounding off errors but serve as a useful check.

The error sum of squares was obtained from the computer print out for the dependent variable cracks/10 mm and the five independent variables

$$\text{error sum of squares} = \underline{268404} = (d)$$

The sum of squares for regression on the five independent variables was obtained by

$$\text{total sum of squares} - \text{error sum of squares}$$
$$= (e) - (d) = (c)$$
$$= 774180 - 268404 = 505776$$

The sum of squares for regression on the two independent variables was calculated from

total sum of squares - error sum of squares.

The error sum of squares was obtained from the computer print out for the dependent variable cracks/10 mm and the two independent variables

774180 - 322096 = 452084

(e) - print out = (a)

The extra variation contributed by the squares of current density and fluoride concentration together with the symmetry term (current density) x (fluoride concentration) was given by the sums of squares contributed by the five independent variables minus the sum of squares contributed by the two independent variables

505776 - 452084 = 53692

(c) - (a) = (b)

TABLE 7.6

ANALYSIS OF VARIANCE TABLES FOR LITHIUM FLUORIDE

Dependent Variable CRACKS (cracks/10 mm)

Source of variation	Degrees of Freedom	Sum of squares	Mean square	F
(a) Regression on CURDEN and CONCEN	2	452084		
(b) Extra contributed by CURDN2, CONCN2 and CURCON	3	53692	17897	2.67
(c) Regression on CURDEN, CONCEN, CURDN2, CONCN2, and CURCON	5	505776		
(d) Error	40	268404	6710	
(e) Total (n = 46)	45	774180		

n = number of points on the regression plane

$$\text{Mean square} = \text{Variance} = \frac{\text{sume of squares}}{\text{degrees of freedom}} = \frac{53692}{3} = 17897$$

$$\text{and} \quad \frac{268404}{40} = 6710$$

Variance ratio = F test = b/d

$$\frac{17897}{6710} = 2.67 = F$$

with 3 and 40 degrees of freedom for the greater and lesser mean square respectively.

This ratio is <u>not</u> significant at the 5% level.

Dependent Variable SPACES (reciprocal of cracks/10 mm)

Source of variation	Degrees of freedom	Sum of squares	Mean square	F
(a) Regression on CURDEN and CONCEN	2	0.0098432		
(b) Extra contributed by CURDN2, CONCN2 and CURCON	3	0.0022861	0.0007620	12.42
(c) Regression on CURDEN, CONCEN, CURDN2, CONCN2, and CURCON	5	0.0121293		
(d) Error	40	0.00245343	0.000061336	
(e) Total (n = 46)	45	0.0145827		

$$\text{F test} = \frac{0.0007620}{0.000061336} = \underline{12.42 = F}$$

with 3 and 40 degrees of freedom respectively.

This ratio is significant at the 1% level.

Dependent Variable LGCRAK (log$_{10}$ cracks/10 mm)

Source of variation	Degrees of freedom	Sum of squares	Mean square	F
(a) Regression on CURDEN and CONCEN	2	7.19457		
(b) Extra contributed by CURDN2, CONCN2 and CURCON	3	0.95995	0.319983	7.45
(c) Regression on CURDEN, CONCEN, CURDN2, CONCN2, and CURCON	5	8.15452		
(d) Error	40	1.71839	0.042959	
(e) Total (n = 46)	45	9.872910		

$$\text{F test} = \frac{0.319983}{0.042959} = 7{,}45 = F$$

with 3 and 40 degrees of freedom respectively.

This ratio is significant at the 1% level.

Dependent Variable CRACK2 (the square of cracks/10 mm)

Source of variation	Degrees of freedom	Sum of squares	Mean square	F
(a) Regression on CURDEN and CONCEN	2	51570413322		
(b) Extra contributed by CURDN2, CONCN2 and CURCON	3	7847100000	2615700000	1.50
(c) Regression on CURDEN, CONCEN, CURDN2, CONCN2 and CURCON	5	59417513322		
(d) Error	40	69802500000	1745062500	
(e) Total (n = 46)	45	129220013322		

$$\text{F test} = \frac{2615700000}{1745062500} = 1.50 = F$$

with 3 and 40 degrees of freedom respectively.

The ratio is not significant at the 10% level

TABLE 7.7

ANALYSIS OF VARIANCE TABLES FOR LITHIUM FLUOROSILICATE

Dependent variable CRACKS (cracks/10 mm)

Source of variation	Degrees of freedom	Sum of squares	Mean square	F
(a) Regression on CURDEN and CONCEN	2	3964005		
(b) Extra contributed by CURDN2, CONCN2 and CURCON	3	2677780	892593	19.21
(c) Regression on CURDEN, CONCEN, CURDN2, CONCN2 and CURCON	5	6641785		
(d) Error	132	6133410	46465	
(e) Total (n = 138)	137	12775195		

$$\text{F test} = \frac{892593}{46465} = 19.21 = F$$

with 3 and 132 degrees of freedom respectively.
The ratio is significant at the 1% level.

Dependent Variable SPACES (reciprocal pf cracks/10 mm)

Source of variation	Degrees of freedom	Sum of squares	Mean square	F
(a) Regression on CURDEN and CONCEN	2	0.00360918		
(b) Extra contributed by CURDN2, CONCN2 and CURCON	3	0.00312737	0.00104245	17.36
(c) Regression on CURDEN, CONCEN, CURDN2, CONCN2, and CURCON	5	0.00673655		
(d) Error	132	0.00792793	0.00006006	
(e) Total (n = 138)	137	0.01466448		

$$\text{F test} = \frac{0.00104245}{0.00006006} = 17.36 = F$$

with 3 and 132 degrees of freedom respectively.
The ratio is significant at the 1% level.

Dependent Variable LGCRAK ($\log_{10}$ cracks/10 mm)

Source of variation	Degrees of freedom	Sum of squares	Mean square	F
(a) Regression on CURDEN and CONCEN	2	9.952438		
(b) Extra contributed by CURDN2, CONCN2 and CURCON	3	6.760310	2.253437	25.21
(c) Regression on CURDEN, CONCEN, CURDN2, CONCN2 and CURCON	5	16.712748		
(d) Error	132	11.7975	0.089375	
(e) Total (n = 138)	137	28.510248		

$$\text{F test} = \frac{2.253437}{0.089375} = 25.21 = F$$

With 3 and 132 degrees of freedom respectively.
The ratio is significant at the 1% level.

Dependent Variable CRACK2 (the square of cracks/10 mm)

Source of variation	Degrees of freedom	Sum of squares	Mean square	F
(a) Regression on CURDEN and CONCEN	2	3149448705792		
(b) Extra contributed by CURDN2, CONCN2, and CURCON	3	2399420000000	799806666666	12.57
(c) Regression on CURDEN, CONCEN, CURDN2, CONCN2, and CURCON	5	5548868705792		
(d) Error	132	8401480000000	63647575757	
(e) Total (n = 138)	137	13950348705792		

$$\text{F test} = \frac{799806666666}{63647575757} = 12.57 = F$$

with 3 and 132 degrees of freedom respectively.
The ratio is significant at the 1% level.

TABLE 7.8

SUMMARY OF ANALYSIS OF VARIANCE RESULTS

Dependent variable	Lithium fluoride	Lithium fluorosilicate
CRACKS	below 5%	1%
SPACES	1%	1%
LGCRAK	1%	1%
CRACK2	below 10%	1%

With two exceptions all the results were significant at the 5% level at least, indicating the importance of introducing five independent variables into the regression equations in order to obtain the best fit. This confirms the results of the analysis of the multiple correlation coefficients.

ANALYSIS OF RESIDUALS

The residuals were analysed to obtain further evidence of the quality of fit of the regression equations to the experimental points. The residuals for lithium fluoride and lithium fluorosilicate were analysed by splitting into three numerically equal parts; lower, middle and upper, then the means and Variances calculated for each part. The Variances of the lower and upper group were then compared by the F test, these two groups being compared since any differences should be largest between these groups. The statistics of the middle group were calculated for visual comparison.

The dependent variable CRACK2, the square of cracks/10 mm, was not included because of the low multiple correlation coefficients.

TABLE 7.9

ANALYSIS OF RESIDUALS

LITHIUM FLUORIDE

Dependent variable CRACKS (cracks/10 mm)

Independent variables CURDEN (current density),
CONCEN (fluoride concentration)

	lower residuals	middle residuals	upper residuals
$\bar{x}$	7.123 ($\bar{x}_1$)	-33.290 ($\bar{x}_2$)	28.387 ($\bar{x}_3$)
V	1200.055	2683.716	16746.678
S.D.	34.642	51.805	129.409
n	15	16	15

where $\bar{x}$ = average

V = variance

S.D. = standard deviation $= \sqrt{V}$

n = number of results

$$\bar{\bar{x}} = \frac{(\bar{x}_1 + \bar{x}_2 + \bar{x}_3)}{3} = 0{\cdot}740$$

$\bar{\bar{x}}$ should = 0 and was a check on the calculations, however it would not be exactly 0 because of rounding off errors.

$$\text{F test} = \frac{16746.678}{1200.055}$$

with 14 and 14 degrees of freedom respectively.
The ratio is significant at the 1% level.

Dependent variable SPACES (reciprocal of cracks/10 mm)

Independent variables CURDEN (current density),
CONCEN (fluoride concentration)

	lower residuals	middle residuals	upper residuals
$\bar{x}$	-0.0024720 ($\bar{x}_1$)	0.0038343 ($\bar{x}_2$)	-0.0016180 ($\bar{x}_3$)
V	0.0001198	0.0001001	0.0000875
S.D.	0.0109453	0.0100049	0.0093541
n	15	16	15

$$\bar{\bar{x}} = -0.0000875$$

F test = 0.0001198/0.0000875 = 1.37

with 14 and 14 degrees of freedom respectively.
The ratio is not significant at the 5% level.

Dependent variable LGCRAK ($\log_{10}$ cracks/10 mm)

Independent variables CURDEN (current density),
CONCEN (fluoride concentration)

	lower residuals	middle residuals	upper residuals
$\bar{x}$	0.0390093 $(\bar{x}_1)$	-0.105137 $(\bar{x}_2)$	0.0733243 $(\bar{x}_3)$
V	0.0289315	0.0267428	0.1136606
S.D.	0.1700926	0.1635322	0.3371358
n	15	16	15

$$\bar{\bar{x}} = 0.0070200$$

$$\text{F test} = \frac{0.1136606}{0.289315} = 3.93$$

with 14 and 14 degrees of freedom respectively.

The ratio is significant at the 1% level.

Dependent variable CRACKS (cracks/10 mm)

Independent variables CURDEN (current density),
CONCEN (fluoride concentration), CURDN2 $(\text{CURDEN})^2$,
CONCN2 $(\text{CONCEN})^2$, CURCON (CURDEN) x (CONCEN)

	lower residuals	middle residuals	upper residuals
$\bar{x}$	-1.6066 $(\bar{x}_1)$	-10.6113 $(\bar{x}_2)$	12.9280 $(\bar{x}_3)$
V	808.7994	3586.3787	12281.2980
S.D.	28.4394	73.3920	110.8210
n	15	16	15

$$\bar{\bar{x}} = 0.7101$$

$$\text{F test} = \frac{12281.2980}{808.7994} = 15.19$$

with 14 and 14 degrees of freedom respectively.

The ratio is significant at the 1% level.

Dependent variable SPACES (reciprocal of cracks/10 mm)

Independent variables CURDEN (current density), CONCEN (fluoride concentration), CURDN2 $(\text{CURDEN})^2$, CONCN2 $(\text{CONCEN})^2$, CURCON (CURDEN) X (CONCEN)

	lower residuals	middle residuals	upper residuals
$\bar{x}$	-0.0008353 $(\bar{x}_1)$	0.0013476 $(\bar{x}_2)$	-0.0006043 $(\bar{x}_3)$
V	0.0000927	0.0000592	0.0000516
S.D.	0.0096280	0.0076941	0.0039496
n	15	16	15

$$\bar{\bar{x}} = -0.0000920$$

$$\text{F test} = \frac{0.0000927}{0.0000516} = 1.80$$

with 14 and 14 degrees of freedom.

The ratio is not significant at the 5% level.

Dependent variable LGCRAK ($\log_{10}$ cracks/10 mm)

Independent variables CURDEN (current density), CONCEN (fluoride concentration), CURDN2 $(\text{CURDEN})^2$, CONCN2 $(\text{CONCEN})^2$, CURCON (CURDEN) x (CONCEN)

	lower residuals	middle residuals	upper residuals
$\bar{x}$	0.0006853 $(\bar{x}_1)$	-0.0260231 $(\bar{x}_2)$	0.0270740 $(\bar{x}_3)$
V	0.0259944	0.0402207	0.0520942
S.D.	0.1612277	0.2005509	0.2282415
n	15	16	15

$$\bar{\bar{x}} = 0.0017362$$

$$\text{F test} = \frac{0.0520942}{0.0259944} = 2.00$$

with 14 and 14 degrees of freedom.

The ratio is not significant at the 5% level.

TABLE 7.10

LITHIUM FLUOROSILICATE

Dependent variable CRACKS (cracks/10 mm)

Independent variables CURDEN (current density),
CONCEN (fluoride concentration).

	lower residuals	middle residuals	upper residuals
$\bar{x}$	-87.074 ($\bar{x}_1$)	160.385	-73.022 ($\bar{x}_3$)
V	11231.986	78322.237	66844.543
S.D.	105.981	279.861	285.543
n	46	46	46

$$\bar{\bar{x}} = 0.288$$

$$\text{F test} = \frac{66844.543}{11231.986} = 5.95$$

with 45 and 45 degrees of freedom.

The ratio is significant at the 1% level.

Dependent variable SPACES (reciprocal of cracks/10 mm)

Independent variables CURDEN (current density),
CONCEN (fluoride concentration).

	lower residuals	middle residuals	upper residuals
$\bar{x}$	0.0019941 ($\bar{x}_1$)	-0.0040839 ($\bar{x}_2$)	0.0020886 ($\bar{x}_3$)
V	0.0001895	0.0000157	0.0000146
S.D.	0.0137658	0.0039623	0.0038209
n	46	46	46

$$\bar{\bar{x}} = 0.0000988$$

$$\text{F test} = \frac{0.0001895}{0.0000146} = 12.98$$

with 45 and 45 degrees of freedom.

The ratio is significant at the 1% level.

Dependent variable LGCRAK ($\log_{10}$ cracks/10 mm)

Independent variables CURDEN (cracks/10 mm),
CONCEN (fluoride concentration).

	lower residuals	middle residuals	upper residuals
$\bar{x}$	-0.1121941 ($\bar{x}_1$)	0.2264856 ($\bar{x}_2$)	-0.1142843 ($\bar{x}_3$)
V	0.1523684	0.1028450	0.0785333
S.D.	0.3903439	0.3206945	0.2802379
n	46	46	46

$$\bar{\bar{x}} = 0.0000072$$

$$\text{F test} = \frac{0.1523684}{0.0785333} = 1.94$$

with 45 and 45 degrees of freedom.

The ratio is significant at the 1% level.

Dependent variable CRACKS (cracks/10 mm)

Independent variables CURDEN (current density),
CONCEN (fluoride concentration), CURDN2 $(\text{CURDEN})^2$,
CONCN2 $(\text{CONCEN})^2$, CURCON (CURDEN) x (CONCEN).

	lower residuals	middle residuals	upper residuals
$\bar{x}$	-19.428 ($\bar{x}_1$)	75.093 ($\bar{x}_2$)	-53.411 ($\bar{x}_3$)
V	14294.094	64141.739	48502.650
S.D.	119.558	253.262	220.233
n	46	46	46

$$\bar{\bar{x}} = 3.254$$

$$\text{F test} = \frac{48502.650}{14294.094} = 3.93$$

with 45 and 45 degrees of freedom.

The ratio is significant at the 1% level.

Dependent variable SPACES (reciprocal of cracks/10 mm)

Independent variables CURDEN (current density), CONCEN (fluoride concentration), CURDN2 $(\text{CURDEN})^2$, CONCN2 $(\text{CONCEN})^2$, CURCON (CURDEN) x (CONCEN)

	lower residuals	middle residuals	upper residuals
$\bar{x}$	-0.0007871 ($\bar{x}_1$)	-0.0005926 ($\bar{x}_2$)	0.0015117 ($\bar{x}_3$)
V	0.0001395	0.0000160	0.0000165
S.D.	0.0118110	0.0040000	0.0040620
n	46	46	46

$$\bar{\bar{x}} = 0.0001320$$

$$\text{F test} = \frac{0.0001395}{0.0000165} = 8.46$$

with 45 and 45 degrees of freedom.

The ratio is significant at the 1% level.

Dependent variable LGCRAK ($\log_{10}$ cracks/10 mm)

Independent variables CURDEN (current density), CONCEN (fluoride concentration), CURDN2 $(\text{CURDEN})^2$, CONCN2 $(\text{CONCEN})^2$, CURCON (CURDEN) x (CONCEN)

	lower residuals	middle residuals	upper residuals
$\bar{x}$	0.0040504 ($\bar{x}_1$)	0.0790091 ($\bar{x}_2$)	-0.0830560 ($\bar{x}_3$)
V	0.1039026	0.0800675	0.0647510
S.D.	0.3223392	0.2829620	0.2544621
n	46	46	46

$$\bar{\bar{x}} = 0.0000035$$

$$\text{F test} = \frac{0.1039026}{0.0647510} = 1.61$$

with 45 and 45 degrees of freedom.

The ratio is not significant at the 5% level.

TABLE 7.11

SUMMARY OF ANALYSIS OF RESIDUALS

Lithium fluoride

Dependent variable	Number of independent variables	
	2	5
CRACKS	1%	1%
SPACES	below 5%	below 5%
LGCRAK	1%	below 5%

Lithium fluorosilicate

Dependent variable	Number of independent variables	
	2	5
CRACKS	1%	1%
SPACES	1%	1%
LGCRAK	1%	below 5%

This analysis showed that when one lot of experimental data was divided into three parts all the parts did not fit the regression equation equally well. In the case of lithium fluoride, dependent variable CRACKS, cracks/10 mm, the F ratio was significant at the 1% level, the situation not being improved by the introduction of five independent variables. Introduction of the dependent variable SPACES, reciprocal of cracks/10 mm, improved the position and the use of LGCRAK $\log_{10}$ cracks/10 mm was also satisfactory with the introduction of five independent variables.

Lithium fluorosilicate was only improved with the use of LGCRAK $\log_{10}$ cracks/10 mm and the introduction of five independent variables.

Statistical analysis so far has shown

1. Analysis of Variance tests indicate that the more complex models give greater accuracy and this is also shown by examination of the Multiple Correlation Coefficients.
2. Analysis of residuals shows better fitting of the experimental results to those calculated from the regression equations for lower values of crack counts, some discrepancies occurring at the higher values. These discrepancies do not occur in all cases.
3. Some transformations of the dependent variable give better fit of experimental results to the regression equations than other transformations.

THE BOX AND COX[90] METHOD

To find the best transformation of the dependent variable the method of Box and Cox[90] was used. This allows the results of one transformation to be directly compared with another.

In this case the dependent variable CRACKS, cracks/10 mm was transformed using the following method

$$\text{Let} \qquad y = \text{CRACKS}$$

$$\text{then} \qquad y^{\lambda} = \frac{y^{\lambda} - 1}{\lambda \dot{y}^{\lambda-1}}$$

where $\dot{y}$ = geometric mean of the original observations

λ = any number in a series from about -3 to +3

Values of λ close to zero were not used in order to avoid possible difficulties with computer calculations, actual values taken were from $\lambda = -2.2$ in increments of +0.5 to $\lambda = +2.3$

The experimental lithium fluoride results for cracks/10 mm were transformed for each of the above values of λ and used in turn as the dependent variable for each of the following two groups of independent variables.

Group I CURDEN current density, CONCEN fluoride concentration

Group II CURDEN current density, CONCEN fluoride concentration, CURDN2 $(\text{CURDEN})^2$, CONCN2 $(\text{CONCEN})^2$, CURCON (CURDEN) x (CONCEN)

The following calculations were done on an Olivetti desk computer before final processing on the ICL 1905 computer.

$$\text{For} \qquad \lambda = -2.2$$

$$y^{\lambda} = \frac{y^{-2.2} - 1}{-2.2\dot{y}^{-2.2-1}} = \frac{y^{-2.2} - 1}{-2.2\dot{y}^{-3.2}}$$

where $\dot{y}$ = the geometric mean of the original observations and was obtained from the antilog of the mean LGCRAK from the "Print Means" on the computer print out from previous computer runs.

$$\dot{y} = 86.72$$

$$\therefore \quad y^{\lambda} = \frac{(\text{CRACKS})^{-2.2} - 1}{-2.2 \times (86.72)^{-3.2}}$$

The denominator was worked out and its reciprocal calculated.

$$\therefore \quad y^{\lambda} = -723379.6((\text{CRACKS})^{-2.2} - 1)$$

The computer was programmed to calculate the above for every numerical value of cracks/10 millimetres and the transformed data used as the dependent variable for calculation of the regression equations using CURDEN, CONCEN and then CURDEN, CONCEN, CURDN2, CONCN2, CURCON as the independent variables in turn.

The complete series of transformations for lithium fluoride is:

$$y^{\lambda} = -723379.6((\text{CRACKS})^{-2.2} - 1) \qquad \lambda = -2.2$$
$$y^{\lambda} = -100535.9((\text{CRACKS})^{-1.7} - 1) \qquad \lambda = -1.7$$
$$y^{\lambda} = -15293.3((\text{CRACKS})^{-1.2} - 1) \qquad \lambda = -1.2$$
$$y^{\lambda} = -2815.47((\text{CRACKS})^{-0.7} - 1) \qquad \lambda = -0.7$$
$$y^{\lambda} = -1058.43((\text{CRACKS})^{-0.2} - 1) \qquad \lambda = -0.2$$
$$y^{\lambda} = 75.7747((\text{CRACKS})^{0.3} - 1) \qquad \lambda = 0.3$$
$$y^{\lambda} = 3.05101((\text{CRACKS})^{0.8} - 1) \qquad \lambda = 0.8$$
$$y^{\lambda} = 0.20163((\text{CRACKS})^{1.3} - 1) \qquad \lambda = 1.3$$
$$y^{\lambda} = 0.01564((\text{CRACKS})^{1.8} - 1) \qquad \lambda = 1.8$$
$$y^{\lambda} = 0.001314((\text{CRACKS})^{2.3} - 1) \qquad \lambda = 2.3$$

The values of the error sum of squares obtained from the computer print out were plotted against the values of λ with the exception of those transformations giving very high error sum of squares. These high results were of little interest since values of λ giving minimum error were required and their omission from the graph allowed a more accurate plot to be made in the minimum error region (Fig. 7.4, Table 7.12).

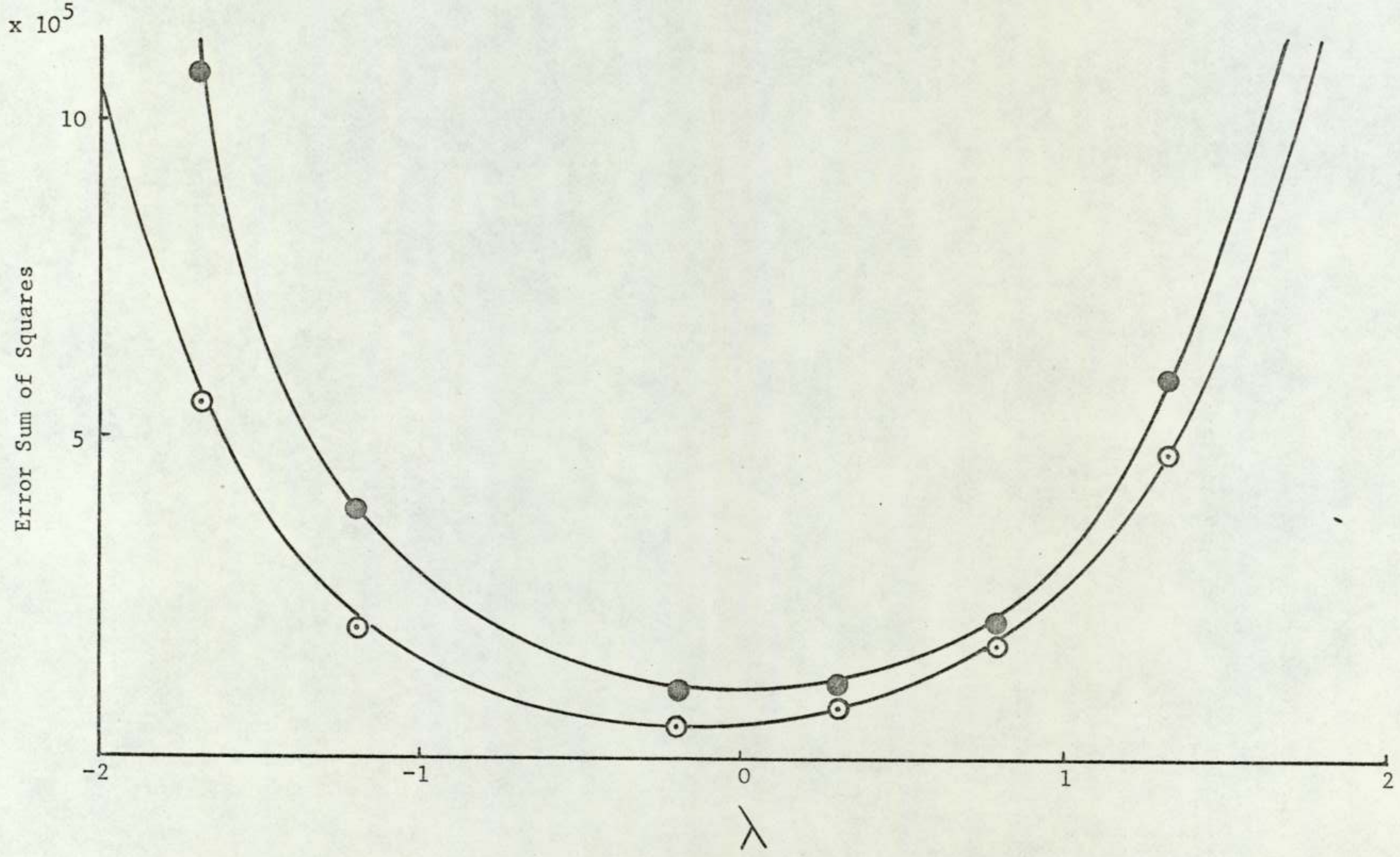

FIG. 7.4. Box and Cox Analysis of Lithium Fluoride Results

The outer parabola included all five independent variables and the inner one only CURDEN, current density and CONCEN, fluoride concentration which confirmed other tests that a more accurate fit of the regression equation to the experimental points is given with five independent variables. The actual value of λ giving minimum error is approximately zero for lithium fluoride.

Rewriting the λ series to the nearest integer gives

$$y^{-2} = \frac{1}{(\mathrm{CRACKS})^2}$$

$$y^{-1} = \frac{1}{\mathrm{CRACKS}} = \mathrm{SPACES}$$

$$y^{0} = \mathrm{LGCRAK}$$

$$y^{1} = \mathrm{CRACKS}$$

$$y^{2} = (\mathrm{CRACKS})^2$$

The best transformation to be applied to this data would be $\lambda = 0$, i.e. the logarithm to base 10 of cracks/10 mm or LGCRAK. The reason for using LGCRAK and not the exact value of λ giving minimum error was because a repeat of the experiment would not give exactly the same results and it would be better to use a natural transformation rather than some arbitrary value of λ.

The value of the multiple correlation coefficient for $\lambda = -0.2$ the nearest transformation to $\log_{10}$ cracks/10 mm, was 0.918, being significant at the 1% level. The t values for the independent variables for $\lambda = -0.2$ are as below.

Independent variable	t
CURDEN	4.71
CONCEN	4.48
CURDN2	2.92
CONCN2	1.27
CURCON	4.42

TABLE 7.12

BOX AND COX ANALYSIS

Lithium Fluoride

Error sum of squares

λ	2 Independent variables	5 Independent variables
- 2.2	3236840	1735720
- 1.7	1072750	562398
- 1.2	388259	199678
- 0.7	168765	88463
- 0.2	108462	64502
0.3	124516	89062
0.8	230879	186672
1.3	564299	485765
1.8	1630380	1451890
2.3	5304520	4823080

Lithium Fluorosilicate

Error sum of squares

λ	2 Independent variables	5 Independent variables
- 1.2	252132000	208629000
- 0.7	51655200	42618000
0.3	12066000	7815330
0.8	8378420	5519200
1.3	11605700	8298920

With the exception of CONCN2, which was not significant at the 5% level, they were all significant at the 1% level at least.

To obtain information on a complex fluoride the above series of calculations were done on the lithium fluorosilicate results, all of the above λ series not being used. The complete series of transformations for lithium fluorosilicate are given below:

$$y^{\lambda} = -271709.6((\mathrm{CRACKS})^{-1.2} - 1) \qquad \lambda = -1.2$$

$$y^{\lambda} = -26011.86((\mathrm{CRACKS})^{-0.7} - 1) \qquad \lambda = -0.7$$

$$y^{\lambda} = -5084.92((\mathrm{CRACKS})^{-0.2} - 1) \qquad \lambda = -0.2$$

$$y^{\lambda} = 189.286((\mathrm{CRACKS})^{0.3} - 1) \qquad \lambda = 0.3$$

$$y^{\lambda} = 3.9362((\mathrm{CRACKS})^{0.8} - 1) \qquad \lambda = 0.8$$

$$y^{\lambda} = 0.136243((\mathrm{CRACKS})^{1.3} - 1) \qquad \lambda = 1.3$$

The values of the error sum of squares obtained from the computer print out were plotted against the values of λ, again all the calculated results were not plotted for the reasons previously given (Fig. 7.5) (Table 7.12). Similar results to those for lithium fluoride were obtained in that minimum error was given when all five independent variables were included. The actual value of λ giving minimum error in this case was about 0.8 and the best natural transformation to use would be $\lambda = 1$, i.e. CRACKS, cracks/10 mm.

The value of the multiple correlation coefficient for $\lambda = 0.8$, the nearest transformation to cracks/10 mm was 0.763, being significant at the 1% level. The t values for the independent variables for $\lambda = 0.8$ are as below:

Independent variable	t
CURDEN	5.58
CONCEN	8.31
CURDN2	5.28
CONCN2	7.16
CURCON	0.66

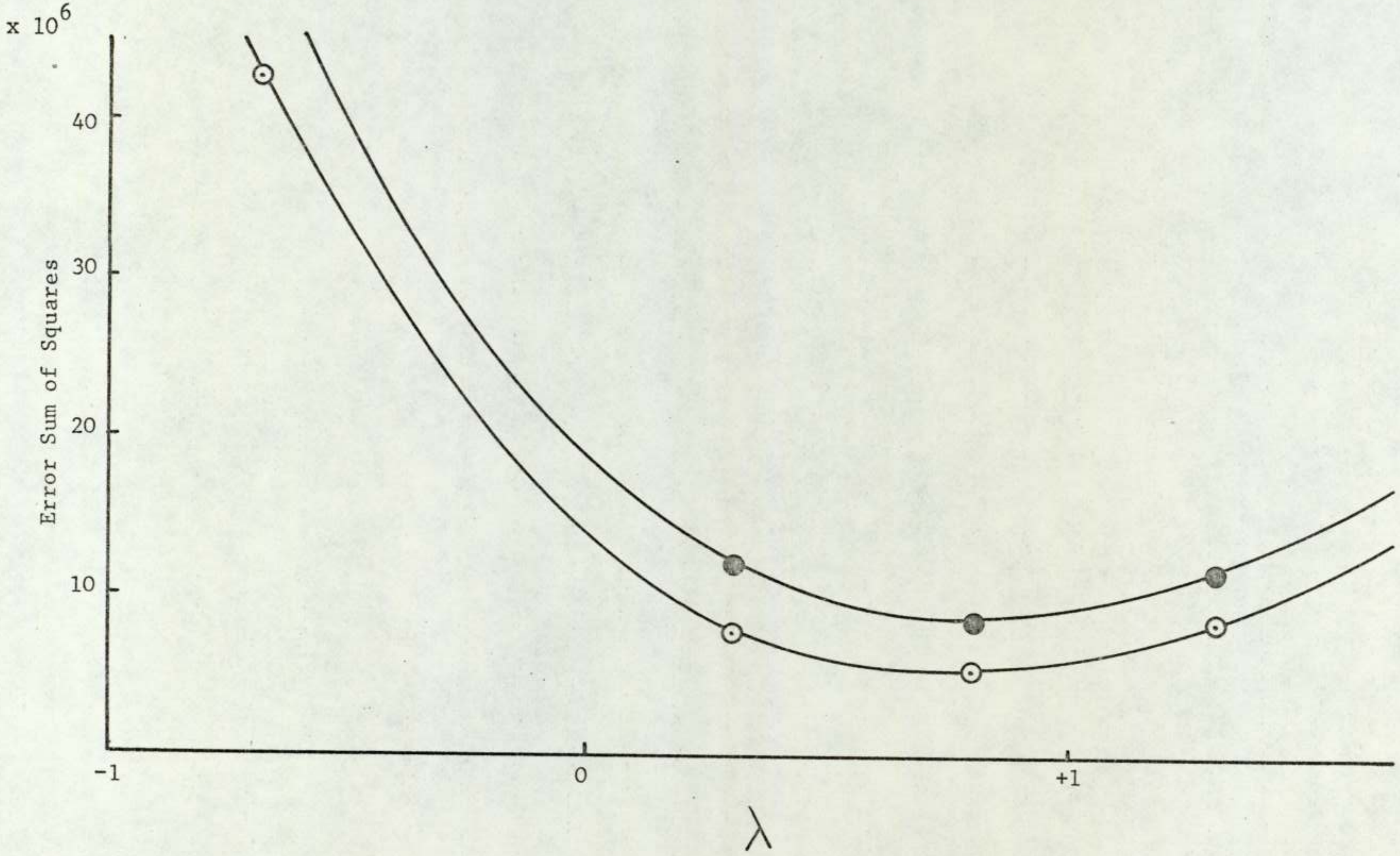

FIG. 7.5. Box and Cox Analysis of Lithium Fluorosilicate Results

With the exception of CURCON which was not significant at the 5% level they were all significant at the 1% level at least.

STATISTICAL ANALYSIS OF COMPLETE DATA

Analysis of the remainder of the data by the Box and Cox[90] method would not be expected to give exactly the same minimum error transformations because of inherent experimental variations. For this reason it was considered justified to use a natural transformation on the remainder of the data rather than some arbitrary number. The transformations used were applied to the original data and the regression models using all the independent variables were calculated.

The dependent variables used on the original data were CRACKS, cracks/10 mm and the transformation LGCRAK, $\log_{10}$ cracks/10 mm for both the simple and complex fluorides since it would be desirable to have directly comparable regression equations for both types of fluoride. The following two models were therefore used to calculate regression equations for all the experimental results

$$\mathrm{CRACKS} = k(\mathrm{CURDEN}) + k_1(\mathrm{CONCEN}) + k_2(\mathrm{CURDN2}) + k_3(\mathrm{CONCN2}) + k_4(\mathrm{CURCON}) + k_5$$

$$\mathrm{LGCRAK} = k(\mathrm{CURDEN}) + k_1(\mathrm{CONCEN}) + k_2(\mathrm{CURDN2}) + k_3(\mathrm{CONCN2}) + k_4(\mathrm{CURCON}) + k_5$$

where CRACKS = cracks/10 mm

LGCRAK = $\log_{10}$ cracks/10 mm

CURDEN = current density in A/dm^2

CONCEN = fluoride concentration in g/l

CURDN2 = $(\mathrm{CURDEN})^2$

CONCN2 = $(\mathrm{CONCEN})^2$

CURCON = (CURDEN) x (CONCEN)

k, k_1, = constants, being different for each equation.

MULTIPLE REGRESSION EQUATIONS

LITHIUM FLUORIDE

$$\begin{aligned}\text{cracks/10mm} = {} & 19.5(\text{current density})+351.5(\text{fluoride concentration}) \\ & -0.14(\text{current density})^2+14.1(\text{fluoride concentration}) \\ & -5.9(\text{current density})(\text{fluoride concentration}) - 577.1\end{aligned}$$

multiple correlation coefficient = 0.808.

$$\begin{aligned}\log_{10}\text{ cracks/10mm} = {} & 0.1126(\text{current density})+1.8528(\text{fluoride concentration}) \\ & -0.0009(\text{current density})^2-0.1103(\text{fluoride concentration})^2 \\ & -0.0256(\text{current density})(\text{fluoride concentration})-1.889\end{aligned}$$

multiple correlation coefficient = 0.909.

LITHIUM FLUOROSILICATE

$$\begin{aligned}\text{cracks/10mm} = {} & 56.3(\text{current density})+1128.5(\text{fluoride concentration}) \\ & -0.85(\text{current density})^2-215.7(\text{fluoride concentration})^2 \\ & -1.48(\text{current density})(\text{fluoride concentration})-1505.4\end{aligned}$$

multiple correlation coefficient = 0.721.

$$\begin{aligned}\log_{10}\text{cracks/10mm} = {} & 0.0819(\text{current density})+1.9575(\text{fluoride concentration}) \\ & -0.0011(\text{current density})^2-0.3762(\text{fluoride concentration})^2 \\ & -0.0038(\text{current density})(\text{fluoride concentration})-0.7349\end{aligned}$$

multiple correlation coefficient = 0.766

SODIUM FLUORIDE

$$\begin{aligned}\text{Cracks/10mm} = {}& -5.0(\text{current density})-42.6(\text{fluoride concentration})\\ &+0.12(\text{current density})^2+109.8(\text{fluoride concentration})^2\\ &-2.7(\text{current density})(\text{fluoride concentration})+78.7\end{aligned}$$

multiple correlation coefficient = 0.726

$$\begin{aligned}\log_{10}\text{ cracks/10mm} = {}& 0.0095(\text{current density})+0.7933(\text{fluoride concentration})\\ &+0.0003(\text{current density})^2+0.2814(\text{fluoride concentration})^2\\ &-0.0232(\text{current density})(\text{fluoride concentration})+0.5525\end{aligned}$$

multiple correlation coefficient = 0.849

SODIUM FLUOROSILICATE

$$\begin{aligned}\text{cracks/10mm} = {}& 41.4(\text{current density})-278.8(\text{fluoride concentration})\\ &-0.60(\text{current density})^2+165.5(\text{fluoride concentration})^2\\ &-3.3(\text{current density})(\text{fluoride concentration})-370.8\end{aligned}$$

multiple correlation coefficient = 0.850

$$\begin{aligned}\log_{10}\text{ cracks/10mm} = {}& 0.0432(\text{current density})+0.4429(\text{fluoride concentration})\\ &-0.0004(\text{current density})^2+0.0673(\text{fluoride concentration})^2\\ &-0.0073(\text{current density})(\text{fluoride concentration})+0.5114\end{aligned}$$

multiple correlation coefficient = 0.931

POTASSIUM FLUORIDE

$$\begin{aligned}\text{cracks/10mm} = {} & -3.2(\text{current density})-92.4(\text{fluoride concentration})\\ & +0.08(\text{current density})^2+115.9(\text{fluoride concentration})^2\\ & -2.1(\text{current density})(\text{fluoride concentration})+81.5\end{aligned}$$

multiple correlation coefficient = 0.821

$$\begin{aligned}\log_{10}\text{cracks/10mm} = {} & 0.0156(\text{current density})+0.2149(\text{fluoride concentration})\\ & +0.0002(\text{current density})^2+0.4632(\text{fluoride concentration})^2\\ & -0.0196(\text{current density})(\text{fluoride concentration})+0.73400\end{aligned}$$

multiple correlation coefficient = 0.868

POTASSIUM FLUOROSILICATE

$$\begin{aligned}\text{cracks/10mm} = {} & 45.1(\text{current density})+385.0(\text{fluoride concentration})\\ & -0.75(\text{current density})^2-47.8(\text{fluoride concentration})^2\\ & +1.4(\text{current density})(\text{fluoride concentration})-808.2\end{aligned}$$

multiple correlation coefficient = 0.853

$$\begin{aligned}\log_{10}\text{cracks/10mm} = {} & 0.0563(\text{current density})+0.8314(\text{fluoride concentration})\\ & -0.0008(\text{current density})^2-0.0916(\text{fluoride concentration})^2\\ & -0.0007(\text{current density})(\text{fluoride concentration})+0.3426\end{aligned}$$

multiple correlation coefficient = 0.861

RUBIDIUM FLUORIDE

$$\begin{aligned}\text{cracks/10mm} = {} & -6.4(\text{current density})-107.1(\text{fluoride concentration}) \\ & +0.08(\text{current density})^2+23.2(\text{fluoride concentration})^2 \\ & +3.9(\text{current density})(\text{fluoride concentration}) + 135.4\end{aligned}$$

multiple correlation coefficient = 0.800

$$\begin{aligned}\log_{10} \text{cracks/10mm} = {} & -0.0094(\text{current density})-0.1421(\text{fluoride concentration}) \\ & +0.0002(\text{current density})^2+0.0224(\text{fluoride concentration})^2 \\ & +0.017(\text{current density})(\text{fluoride concentration})+1.3664\end{aligned}$$

multiple correlation coefficient = 0.776

CAESIUM FLUORIDE

$$\begin{aligned}\text{cracks/10mm} = {} & 3.8(\text{current density})+329.6(\text{fluoride concentration}) \\ & +0.01(\text{current density})^2-110.7(\text{fluoride concentration})^2 \\ & -3.7(\text{current density})(\text{fluoride concentration})-147.6\end{aligned}$$

multiple correlation coefficient = 0.606

$$\begin{aligned}\log_{10} \text{cracks/10mm} = {} & 0.0392(\text{current density})+2.7797(\text{fluoride concentration}) \\ & -0.001(\text{current density})^2-0.9029(\text{fluoride concentration})^2 \\ & -0.0350(\text{current density})(\text{fluoride concentration})-0.1254\end{aligned}$$

multiple correlation coefficient = 0.732

CAESIUM FLUOROSILICATE

$$\text{cracks/10 mm} = 93.0(\text{current density})+1838.2(\text{fluoride concentration})$$
$$-1.6(\text{current density})^2-630.2(\text{fluoride concentration})^2$$
$$+15.1(\text{current density})(\text{fluoride concentration})-2647.1$$

multiple correlation coefficient = 0.864

$$\log_{10}\text{cracks/10mm} = 0.11(\text{current density})+4.0(\text{fluoride concentration})$$
$$-0.002(\text{current density})^2-1.2(\text{fluoride concentration})^2$$
$$+0.01(\text{current density})(\text{fluoride concentration})-2.861$$

multiple correlation coefficient = 0.934

AMMONIUM FLUORIDE

$$\text{cracks/10mm} = 2.8(\text{current density})+137.2(\text{fluoride concentration})$$
$$-0.01(\text{current density})^2-47.6(\text{fluoride concentration})^2$$
$$-0.76(\text{current density})(\text{fluoride concentration})-96.7$$

multiple correlation coefficient = 0.533

$$\log_{10}\text{cracks/10mm} = 0.0347(\text{current density})+1.4535(\text{fluoride concentration})$$
$$-0.0002(\text{current density})^2-0.4962(\text{fluoride concentration})^2$$
$$-0.0084(\text{current density})(\text{fluoride concentration})+0.0349$$

multiple correlation coefficient = 0.533

AMMONIUM FLUOROSILICATE

$$\begin{aligned} \text{cracks/10mm} = {} & 55.0(\text{current density})+700.5(\text{fluoride concentration}) \\ & -0.83(\text{current density})^2-132.3(\text{fluoride concentration})^2 \\ & +2.3(\text{current density})(\text{fluoride concentration})-1200.7 \end{aligned}$$

multiple correlation coefficient = 0.870

$$\begin{aligned} \log_{10} \text{cracks/10mm} = {} & 0.0598(\text{current density})+1.1273(\text{fluoride concentration}) \\ & -0.0008(\text{current density})^2-0.1790(\text{fluoride concentration})^2 \\ & -0.0006(\text{current density})(\text{fluoride concentration})+0.1757 \end{aligned}$$

multiple correlation coefficient = 0.746

HYDROFLUOROSILICIC ACID

$$\begin{aligned} \text{cracks/10mm} = {} & 47.3(\text{current density})+532.8(\text{fluoride concentration}) \\ & -0.7(\text{current density})^2-113.8(\text{fluoride concentration})^2 \\ & +2.6(\text{current density})(\text{fluoride concentration})-988.9 \end{aligned}$$

multiple correlation coefficient = 0.879

$$\begin{aligned} \log_{10} \text{cracks/10mm} = {} & 0.0854(\text{current density})+1.4936(\text{fluoride concentration}) \\ & -0.0011(\text{current density})^2-0.2871(\text{fluoride concentration})^2 \\ & -0.0002(\text{current density})(\text{fluoride concentration})-0.6086 \end{aligned}$$

multiple correlation coefficient = 0.914

The multiple correlation coefficients for all these equations were significant at the 1% level at least, including those for rubidium fluoride and potassium fluorosilicate. The data from these two fluorides was not considered very reliable because of insufficient experimental results for rubidium fluoride and the insolubility of potassium fluorosilicate at the higher concentrations.

The high values of the coefficients confirmed the results of the previous analysis that the best fit of the regression equations to the experimental points would be given by either cracks/10 mm or $\log_{10}$ cracks/10 mm as the dependent variable and the inclusion of all five independent variables, although the regression equation with the highest multiple correlation coefficient did not necessarily have the minimum error sum of squares.

The goodness of fit of a calculated regression equation to the experimental points may be illustrated by plotting a graph of crack counts calculated using the regression equation against the experimental crack counts. This is illustrated for the results of lithium fluoride with the dependent variable cracks/10 mm.

The 95% confidence limits are given by:

$$Y = \hat{y} \pm \text{residual error of } y \times t_v$$

where t_v is the appropriate value of t for v degrees of freedom.

t_v = 2.02 (with 40 degrees of freedom at the 2.5% level, i.e. a total of 5% for both sides of the line or 95% confidence limits).

residual error = 81.9 (from computer print out)

$$\therefore \quad Y = \hat{y} \pm 81.9 \times 2.02$$

$$\therefore \quad Y = \hat{y} \pm 165 \text{ cracks/10 mm.}$$

The results are illustrated graphically in Fig. 7.6 and it should be noted that out of a total of forty-six results only one lies outside the 95% confidence limits. For ease of illustration groups of points lying close together are illustrated by bars.

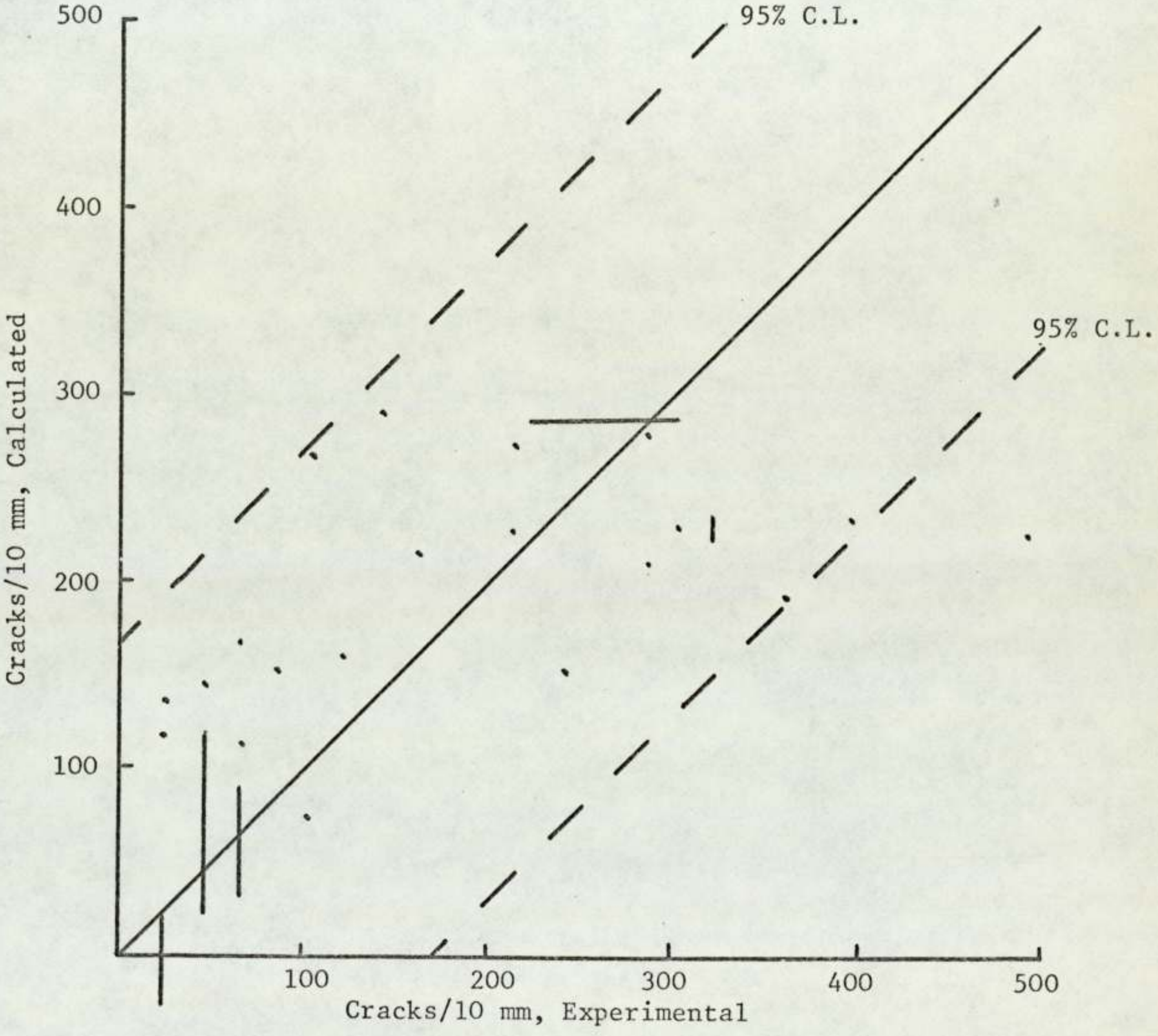

FIG. 7.6. 95% Confidence Limits for Lithium Fluoride Results

COMBINATION OF DATA

It would be desirable to combine all the data in one regression equation but this was not considered possible particularly for the different types of fluorides. However it should be possible to combine the data for lithium, sodium, potassium and caesium fluorides and for lithium, sodium and caesium fluorosilicates. Rubidium fluoride and rubidium fluorosilicate were not included because of lack of sufficient data due to the expense of rubidium salts, neither was potassium fluorosilicate because of its insolubility at higher concentrations.

The dependent variables used were $\log_{10}$ cracks/10 mm for the simple fluorides and cracks/10 mm for the fluorosilicates since these gave minimum error in the Box and Cox analysis, five independent variables being used in both cases.

The regression equation for lithium, sodium, potassium and caesium fluorides was

$$\begin{aligned}\log_{10} \text{cracks/10mm} = {} & 0.0011(\text{current density})+0.2111(\text{fluoride concentration}) \\ & +0.0003(\text{current density})^2+0.3360(\text{fluoride concentration})^2 \\ & -0.0128(\text{current density})(\text{fluoride concentration})+1.1467\end{aligned}$$

The multiple correlation coefficient of 0.796 was significant at the 1% level at least. The t values are as below:

Regression coefficient	t value	significance level
current density	0.13	below 5%
fluoride concentration	1.21	below 5%
$(\text{current density})^2$	2.55	1% at least
$(\text{fluoride concentration})^2$	5.43	1% at least
(current density)(fluoride concentration)	4.67	1% at least

The current density and fluoride concentration coefficients were not significant but were included to reduce overall error. This does not mean that current density and fluoride concentration were without effect on cracks/10 mm since the square of both these terms had a t value significant at the 1% level at least.

The regression equation for lithium, sodium and caesium fluorosilicates was

$$\begin{aligned}\text{cracks/10 mm} = {} & 48.1(\text{current density})+912.9(\text{fluoride concentration}) \\ & -0.70(\text{current density})^2-149.0(\text{fluoride concentration})^2 \\ & -1.85(\text{current density})(\text{fluoride concentration})-1269.8\end{aligned}$$

The multiple correlation coefficient of 0.720 was significant at the 1% level at least. The t values are as below:

Regression coefficient	t value	significance level
current density	5.17	1% at least
fluoride concentration	7.93	1% at least
(current density)^2	4.90	1% at least
(fluoride concentration)^2	5.88	1% at least
(current density)(fluoride concentration)	0.88	below 5%

The only regression coefficient not significant was (current density)(fluoride concentration), the symmetry term, but it was included to reduce overall error.

EFFECT OF THE ALKALI METALS

Since initial analysis showed the most important independent variable to be fluoride concentration other parameters were looked for in place of or as well as fluoride concentration. Linear regression analysis was done with atomic number, atomic weight, atomic radius and ionic radius taken in turn as the independent variable with the regression coefficients for fluoride concentration as the dependent variable. The regression equation from which the dependent variables were taken was

$$\text{CRACKS} = k\,(\text{CURDEN}) + k_1(\text{CONCEN}) + k_2$$

where k_1 = the dependent variable coefficient taken.

Data from this simple model was used because it was desirable to concentrate all the fluoride concentration effects into a single coefficient although it was known that this simple model would not give such a good fit of the regression equation to the experimental results as a more complex one.

The results for lithium, sodium, potassium and caesium fluorides are given in Table 7.13.

TABLE 7.13

Dependent variable		Independent variables			
	Regression coefficient	Atomic number	Atomic weight	Ionic radius	Atomic radius
LiF	171.4	3	7	0.78	1.56
NaF	114.7	11	23	0.98	1.86
KF	103.9	19	39	1.33	2.23
CsF	65.3	55	133	1.65	2.55
r		-0.886	-0.863	-0.939	-0.959

For two degrees of freedom atomic radius was the only parameter significant above the 5% level.

A similar analysis was done for lithium, sodium and caesium fluorosilicates and the results are in Table 7.14.

TABLE 7.14

Dependent variable		Independent variables			
	Regression coefficient	Atomic number	Atomic weight	Ionic radius	Atomic radius
Li_2SiF_6	244.1	3	7	0.78	1.56
Na_2SiF_6	310.5	11	23	0.98	1.86
Cs_2SiF_6	498.0	55	133	1.65	2.55
		0.994	0.990	0.999	0.999

For one degree of freedom ionic radius and atomic radius were significant at the 5% level and for comparison with the simple fluorides atomic radius was used for further analysis.

Atomic radii of the alkali metals were found to be related to fluoride concentration for both simple and complex fluorides and the following model was therefore built up.

$$\text{CRACKS} = k + x(\text{CONCEN})$$

where $\text{CRACKS} = \text{cracks/10 mm}$

$\text{CONCEN} = \text{fluoride concentration}$

$k, k_1, k_2 \ldots = \text{constants}$

$x = \text{a term containing atomic radius}$

$$\therefore \quad \text{CRACKS} = k + k_1(\text{atomic radius})(\text{fluoride concentration})$$

A less simple model was also built up

$$\text{CRACKS} = k + k_1\ (k_2(\text{atomic radius}) + k_3)\ (\text{fluoride concentration})$$

$$\therefore \quad \text{CRACKS} = k + (k_4(\text{atomic radius}) + k_5) + k_5)(\text{fluoride concentration})$$

CRACKS = $k + k_4$(atomic radius)(fluoride concentration)+k_5(fluoride concentration)

The following regression equations were calculated using the computer.

LITHIUM, SODIUM, POTASSIUM AND CAESIUM FLUORIDES

cracks/10 mm = 51.4 (atomic radius)(fluoride concentration) - 25.9

The multiple correlation coefficient of 0.545 was significant at the 1% level at least and the t value for the regression coefficient was significant at the 0.1% level.

Cracks/10 mm = 185.3(fluoride concentration) - 40.6 (atomic radius) (fluoride concentration) - 27.8

The multiple correlation coefficient of 0.674 was significant at the 1% level at least and the t values for the regression coefficients were significant at the 0.1% level.

LITHIUM, SODIUM AND CAESIUM FLUOROSILICATES

cracks/10 mm = 151.8 (atomic radius)(fluoride concentration) - 70.4

The multiple correlation coefficient of 0.618 was significant at the 1% level at least and the t value for the regression coefficient was significant at the 0.1% level.

cracks/10 mm = 194.7 (fluoride concentration) + 57.3 (atomic radius) (fluoride concentration) - 110.5

The multiple correlation coefficient of 0.646 was significant at the 1% level at least and the t values for the regression coefficients were significant at the 0.1% level.

Higher multiple correlation coefficients were obtained with the more complex models, indicating a better fit for both simple and complex fluorides although there was adequate fit with the simpler model.

It may be argued that for both types of fluorides the concentration effect, which was known to be large, masked the effect of the atomic radius. The following regression equation was therefore used to investigate this

$$\text{cracks/10 mm} = k(\text{atomic radius}) + k_1$$

LITHIUM, SODIUM, POTASSIUM AND CAESIUM FLUORIDES

$$\text{cracks/10 mm} = -76.6(\text{atomic radius}) + 247.3$$

The correlation coefficient of 0.298 was significant at the 1% level at least and the t value for the regression coefficient was significant at the 0.1% level.

LITHIUM, SODIUM AND CAESIUM FLUOROSILICATES

$$\text{cracks/10 mm} = -39.2(\text{atomic radius}) + 481.5$$

$$\text{correlation coefficient} = 0.042$$

Neither the correlation coefficient nor the t value for the regression coefficient was significant at the 5% level for the fluorosilicates.

In the case of the complex fluorides there was no correlation between cracks/10 mm and atomic radius suggesting that the fluoride concentration effect masks the atomic radius effect. There was however ample evidence to show that some parameter of the alkali metals, in this case atomic radius, had an effect on microcracking particularly in the case of the simple fluorides.

With the complex fluorides correlation was obtained between cracks/10 mm and fluoride concentration together with atomic radius it appears that the concentration effect masks the atomic radius effect. A general equation involving both fluoride concentration and atomic radius should not therefore be built up.

CHAPTER 8

THEORETICAL DISCUSSION AND CONCLUSIONS

It appears that the non fluoride parts of catalysts influence microcracking because equivalent fluoride concentrations of different fluoride catalysts do not give the same results. At equivalent fluoride concentrations simple compounds such as lithium fluoride do not give the same results as more complex ones such as lithium fluorosilicate.

Under the conditions used chromium plating solutions in polythene containers and with simple fluoride additions did not give microcracked deposits. The same solutions under identical conditions but used in glass containers did give microcracked deposits. This implies that a reaction product formed from glass and a fluoride is responsible for microcracking in this case.

The use of reaction products as catalysts has been reported by Spencer[55], a chromium compound, an organic reducing agent and hydrofluosilicic acid all being reacted together to form catalysts.

The following mechanism is proposed for the formation of a reaction product between glass and a chromium plating solution containing a simple fluoride.

In the solutions of pH below four, fluoride ions will combine with hydrogen ions giving hydrofluoric acid[24]. Hood[52] reported the formation of free hydrofluoric acid during the use of fluoride addition agents in chromium plating solutions. The free acid so formed will attack glass forming silicon tetrafluoride which then reacts with water forming hydrofluosilicic[75] acid.

These reactions may be summarised

$$F^- + H^+ \rightleftharpoons HF$$

$$4\ HF + SiO_2 \longrightarrow 2\ H_2O + SiF_4$$

$$2\ SiF_4 + 2\ H_2O \longrightarrow 2\ H_2SiF_6 + SiO_2$$

For the reactions to proceed along the above lines the presence of insoluble silica should be detected. Initial experimental work on solutions containing potassium fluoride in glass containers when used for periods of at lest twenty-four hours developed a deposit of silica at the bottom of the container which was confirmed by chemical analysis[60]. Silica has been shown to be a breakdown product of silicofluoride catalysts[76], although the presence of sulphate reduces the amount of such breakdown. Hood[52] reported that although the presence of sulphuric acid reduced fluoride catalyst breakdown it did not do so entirely.

The fact that the presence of a silicon compound was necessary to cause microcracking was confirmed by microcracked deposits being obtained from chromium plating solutions containing fluorosilicate additions when used in plastic beakers.

Since hydrofluosilicic acid causes somewhat different microcracking from that of reaction products of simple fluorides with glass it is likely that such products may not be entirely hydrofluosilicic acid. It is also probable that mixtures of unreacted fluorides and reaction products modify the microcracking.

Whatever these breakdown products are their mode of action is dependent on the alkali metal originally present. This is confirmed by the quantitative relationships established between various parameters of the alkali metals and results derived from crack counts.

Since breakdown of silicofluorides[24,76] has been shown to occur the following mechanism is suggested

$$H_2SiF_6 \rightleftharpoons SiF_4 + 2\,HF$$

$$3\,SiF_4 + 2\,H_2O \longrightarrow 2\,H_2SiF_6 + SiO_2$$

It is most likely that no single mechanism is responsible for the breakdown of any fluoride, rather a series of complex reactions occurring.

A catalyst[77] is unchanged chemically at the end of the reaction and since breakdown of fluorides occurs, if only slowly, they are not acting as true catalysts and it is incorrect to call them such.

It appears that sulphuric acid acts as a true catalyst there being no reports in the literature of sulphate breakdown. Further, results[78] of chemical analyses of a chromium plating solution over several years show no change in sulphate concentration.

FATE OF REACTION PRODUCTS

These suggestions are made as to the fate of fluoride reaction products. Some of the evolved hydrofluoric acid could escape into the atmosphere and Hood[52] reported pitting corrosion of electroplated work due to the presence of this acid. The free silica which is formed and whose presence has been experimentally confirmed could react with the acid

$$4\ HF + SiO_2 \longrightarrow 2\ H_2O + SiF_4$$

or

$$6\ HF + SiO_2 \longrightarrow H_2SiF_6 + 2\ H_2O$$

The fate of these products is of course intimately tied up with the formation of glass/fluoride reaction products as previously discussed.

There is also the possibility of incorporation of reaction products and/or other material into the electrodeposit. The presence of neither potassium nor rubidium was detected in chromium deposits obtained from solutions containing fluoride compounds of these elements. It is not possible from these results to prove the complete absence of either potassium or rubidium but if they are present it will be at a very low level, presumably of the same order as the fluorine at about 0.01%.

The presence of fluorine was detected in the bulk of the electrodeposit at a level of 0.01% and in the surface layers it was about 0.2%. This high surface percentage should be treated with some reservation since it could be an adsorption effect and further work is necessary. Should 0.2% be confirmed then probably fluorine diffuses outwards from the inner layers remaining concentrated in the surface on cessation of plating. An alternative explanation is that the fluorine concentrated in the outer layers influences the cyclic cracking and healing processes[29,42].

Since simple fluorides did not cause microcracking and silicofluorides did then it is suggested that silicon is also codeposited at a level of about 0.01%. Complexes similar to $SiF_6^{=}$ could be responsible for distortion of the chromium lattice resulting in stress of the electrodeposit which is then relieved by microcracking.

The ratio of metallic chromium to fluoride ions in a chromium plating solution containing 150 gms/l chromic acid and 1.358 gms/l fluoride ion (3.0 gms/l NaF) may be calculated

$$150 \text{ gms chromic acid} = 150 \times \frac{\text{atomic weight Cr}}{\text{molecular weight } CrO_3}$$

$$= 150 \times \frac{52}{100} = 78.0$$

$$\text{Ratio of Cr to F} = \frac{78.0}{1.358} = \frac{57.44}{1} = \frac{100}{1.74}$$

On the assumption that the rates of metallic chromium and fluoride ion deposition are the same then the metal deposit will contain about 2% fluoride. This calculation must give a high result because it is not possible to electrodeposit fluorine from aqueous solutions[61] and codeposition of fluoride ions with chromium would therefore be expected to be difficult. In any event commercial chromium plating solutions have very long lives suggesting that fluoride breakdown is very slow.

EFFECTS OF DIFFERENT FLUORIDES

The different results obtained from equivalent fluoride concentrations for simple and complex fluorides of the same alkali metal may be attributed to:

1. the reaction products of a simple fluoride and glass being different from the same alkali metal complex fluoride, e.g. reaction products of lithium fluoride and glass do not give pure lithium fluorosilicate but a mixture of lithium fluorosilicate and similar compounds. There is also the likelihood that reaction products of simple fluorides and glass are not the same as reaction products of simple fluorides and pure silica. The presence of "impurities" introduced from glass could explain differences between the effects of complex fluorides and reaction products of simple fluorides and glass.
2. the reaction products of simple fluorides and glass are similar to complex fluorides in that they both cause microcracking.
3. microcracking is caused by (a) a mixture of a simple fluoride and a reaction product, (b) a complex fluoride such as lithium fluorosilicate.
4. complex fluorides cause microcracking without the need to form a reaction product with glass although it has been shown that breakdown of complex fluorides does occur, if only slowly, in the absence of glass.

DIFFERENCES CAUSED BY ALKALI METALS, HYDROGEN AND AMMONIUM IONS

1. Fixed current density cathodes

The effects of simple and complex fluorides will be treated separately because of their different effects on microcracking.

With both types of fluorides of the alkali metals quantitative relationships exist between a measure of the rate of change of fluoride concentration with crack density and parameters of the alkali metals such as atomic number (Table 6.3). Ammonium fluoride and ammonium fluorosilicate would not be expected to follow the same pattern as the alkali metals because of the obvious differences between ammonium (NH_4) and the alkali metals. Hydrofluosilicic acid is included with the complex fluorides because hydrogen may be placed at the head of the alkali metals in the periodic table.

The effect of caesium is apparently anomalous since it does not follow the same general pattern as the other alkali metals.

Solubilities (Table 6.5) show a regular pattern for simple fluorides with increasing solubility for increasing molecular weight, no such regular pattern is shown by the complex fluorides. Caesium fluoride is roughly 100 times more soluble than lithium fluoride the converse being true for caesium and lithium fluorosilicates. The apparently anomalous behaviour of caesium cannot be accounted for by examination of the fluoride solubilities. However the solubilities will be altered by the large amount of chromic acid present and it must be remembered that it is the reaction products of the simple fluorides and glass that cause microcracking. Not too much emphasis should therefore be placed on deductions from direct solubility effects.

Since for both simple and complex fluorides it is the caesium compounds that show anomalous behaviour it may be inferred that some property of the element caesium is the cause. Examination of properties of the alkali metals (Table 6.4) shows that caesium follows the same general pattern there being no obvious differences to account for its behaviour.

To speculate on the behaviour of caesium it may be that some surface property of the alkali metals may show that caesium is not in an anomalous position with respect to microcracking but that it then fits the same general pattern as the other alkali metals.

It has been assumed so far that concentrations are equal to activities so to be strictly accurate concentrations should be replaced by activities.

Frant[79] found that the activities of fluorides in the presence of chromic acid were very much reduced. Electrode measurements showed that when F^- was replaced with an equivalent quantity of $SiF_6^=$ a much lower F^- activity resulted, presumably due to part of the fluoride still being complexed as silicofluoride. This suggestion by Frant accounts well with the experimental findings that at the higher equivalent fluoride concentrations simple fluorides give much higher crack counts than complex fluorides (Table 6.1).

The activity controlling both the rate and extent of chemical and electrochemical reactions is in this case measured by the extent of microcracking.

The main objection to these arguments was pointed out by Frant who had no independent way of measuring fluoride ion activity in chromium plating solutions. Measurements were made with an electrode previously calibrated in solutions of known fluoride ion activity.

2. Hull cell cathodes and covering power

Covering power is also influenced by the alkali metals as shown previously and some evidence of the anomalous behaviour of caesium found, Fig. 7.1 and Fig. 7.2.

3. Hull cell cathodes and microcracking

It has already been shown p.113-p.163 that quantitative relationships exist between microcracking, fluoride concentration and current density, with fluoride concentration having the most effect on microcracking. Examination of the regression coefficients of Table 7.13 and Table 7.14 shows that for simple fluorides they decrease from lithium fluoride to caesium fluoride and in the case of complex fluorides they increase from lithium to caesium fluorosilicate. This shows the different effects caused by simple and complex fluorides and the undesirability of combining data from both types of fluorides.

The apparently anomalous behaviour of caesium is not shown up by multiple regression analysis. This may in part be due to the incoporation of current density into the analysis, previous results having been obtained from fixed current density cathodes. There is some evidence however that caesium is anomalous when covering power is measured using the Hull Cell

METAL CATHODE EFFICIENCY

The metal cathode efficiency for chromium deposition from chromic acid solutions is considerably lower than for other metal electrodeposition processes, being of the order of 10% to 20%. This is because current is used other than for chromium deposition, being hydrogen evolution and redox reactions. Work has been done on this by Solov'eva et al[28] and Griffin as discussed on pages 7-9. The effect of hydrogen on the initial stages of microcracking is also important as shown by Cleghorn and West[44] and Dennis[42] and discussed on pages 20-24.

INHIBITION OF CHROMIUM PLATING AT LOW AND HIGH FLUORIDE CONCENTRATIONS

Weiner[80] overcame the difficulties of explaining the fact that small additions of sulphate greatly accelerate the dissolving action of chromic acid on the cathode film but that larger sulphate additions diminished this effect. He found that basic chromium compounds were not dissolved by pure chromic acid but by the addition of a small quantity of another anion such as sulphate, chloride, fluoride, the solubility increased rapidly and then decreased with increasing additions. The addition agents greatly accelerated the dissolving action of the chromic acid but a larger addition diminished this influence and this was a chemical not an electrochemical effect.

It was observed from this present work (Fig. 6.1) that at the higher fluoride concentrations chromium deposition ceased and in some cases was preceeded by either a diminution or complete cessation of microcracking. This may be due to the chemical insolubility of the cathode film in chromic acid at the higher fluoride concentrations.

An alternative explanation is that chromium plating is in any case beginning to cease at higher fluoride concentrations as suggested by Weiner[80] and is thus indirectly influencing microcracking.

CONCLUSIONS

1. Chromium electrodeposition only occurs within a narrow range of fluoride concentrations. At zero and high fluoride concentrations deposition does not occur.
2. Microcracking also only occurs within a narrow range of fluoride concentrations, the range being narrower than the one within which chromium plating occurs. That is, microcracking does not occur at very low and very high fluoride concentrations although chromium deposition may do so.
3. A theory for the cessation of microcracking at low and high fluoride concentrations is proposed.
4. Simple fluorides do not cause microcracking.
5. Complex fluorides cause microcracking.
6. Reaction products of simple fluorides with glass cause microcracking.
7. A theory for the formation of reaction products is proposed.
8. The reaction products have a similar effect to those of complex fluorides but there are differences.
9. Microcracking increases linearly with increase of fluoride concentration when measured on constant current density cathodes.
10. Covering power, as measured with a Hull Cell, is influenced by both fluoride concentration and the alkali metal part of the fluoride molecule.
11. Linear quantitative relationships exist between covering power, as measured with a Hull Cell, and fluoride concentration. It should be possible to use these relationships for fluoride control in commercial practice, all other variables remaining constant.
12. Non-linear quantitative relationships exist between microcracking and current density together with fluoride concentration for Hull Cell results, concentration having the greatest effect. These

equations can be used to predict crack counts but only for Hull Cell results over the range of experimental results from which the equations were developed. However it may be possible to develop similar equations for use with commercial solutions by a suitable study of the various parameters. It is not possible to say whether this is economically sound but it should be theroetically possible.

13. All quantitative relationships are affected by the type of fluoride, simple fluorides giving different results from complex ones at equivalent fluoride concentrations.
14. Taking simple and complex fluorides separately the alkali metal part of the molecule profoundly affects microcracking, linear quantitative relationships existing between various parameters of the alkali metals and microcracking.
15. Caesium is apparently anomalous having a much greater effect on microcracking than the other alkali metals.
16. Since fluorides break down during use, if only slowly, it is incorrect to call them catalysts.
17. Since sulphates do not break down and fluorides do, their modes of action must be different although there are probably similarities especially as fluoride breakdown is not very rapid.
18. Some experimental evidence is available for the codeposition of fluorides with microcracked chromium.

SUGGESTED FURTHER WORK

1. A theoretical study of the incorporation of other elements into the structure of electrodeposited chromium.
2. Quantitative determinations of other elements codeposited with the chromium.
3. An investigation into the effect of current supply on microcracking because it is possible to control it on a commercial scale.
4. More work is required on the anomalous behaviour of caesium.
5. Multiple non-linear regression analysis is a powerful tool for investigating relationships between variables, not necessarily with microcracked chromium.
6. An investigation into the life of solutions in contact with glass bearing in mind that unknown composition chemical additions are made to commercial solutions to keep them in balance.

APPENDIX

EXPERIMENTAL RESULTS

CRACK COUNTS/10 mm ON 75 mm x 50 mm CATHODES

Position A   Across the 50 mm width, 25 mm from the bottom of the cathode.

Position B   Down the centre of the 75 mm length beginning from the bottom of the cathode.

LITHIUM FLUORIDE ADDITIONS, GLASS CONTAINER

1.237 g/l   Chromium deposition, no cracking.

1.854 g/l,A   every 2 mm 138, 118, 157, 98, 118, 138, 118, 138, 118, 98, 118, 177, 118, 138, 138, 157, 98, 98, 98, 118,

1.854 g/l,B   every 1 mm 59, 20, 39, 79, 59, 59, 59, 20, 39, 79, 118, 98, 39, 59, 79, 20, 98, 98, 98, 59, 98, 79, 157, 98, 138, 138, 138, 118, 138, 138, 157, 215, 138, 138, 177, 157, 138, 197, 236, 216, 216, 197, 216, 276, 295, 197, 276, 197, 177, 236, 276, 276, 256, 256, 216.

2.471 g/l,A   Difficult to count - estimated 1969

2.471 g/l,B   every 1 mm 236, 334, 394, 511, 590, 610, 708, 846, 826, 1000, 1120, 1040, 1040, 1240, 1320, 1320, 1470, 1470.
Then difficult to count - estimated 1772

2.780 g/l,A   Difficult to count - estimated 1969

2.780 g/l,B   every 1 mm 532, 767, 985, 1040, 1240, 1300, 1240, 1260, 1420, 1340, 1360, 1300
Then difficult to count, estimated 1476

LITHIUM FLUOROSILICATE ADDITIONS, PLASTIC CONTAINER

1.081 g/l,A   every 2mm 0, 0, 35, 0, 0, 0, 0, 0, 0, 35, 0, 35, 35, 35, 0, 35, 35, 35, 0, 0.

1.081 g/l,B	every 2 mm 71, 71, 35, 0, 0, 35, 35, 35, 35, 0, 0, 0, 35, 35, 35, 35, 35, 0, 0, 35, 71, 35, 35, 0, 0, 0, 35, 0, 0, 0, 0, 0.
1.622 g/l,A	every 2 mm 106, 71, 390, 390, 390, 460, 496, 496, 71, 71, 106, 71, 106, 71, 71, 354, 354, 106, 71, 142.
1.622 g/l,A	every 2 mm 177, 142, 248, 284, 248, 284, 284, 142, 177, 106, 71, 0, 106, 0, 71, 35, 35, 319, 284, 71, 106, 106, 35, 142, 71, 71, 71, 0, 106, 212, 71.
2.162 g/l,A	every 2 mm 354, 531, 354, 390, 496, 319, 390, 425, 425, 496, 460, 496, 460, 354, 567, 425, 319, 460, 354, 496.
2.162 g/l,B	every 2 mm 496, 566, 638, 673, 601, 566, 531, 673, 496, 496, 531, 496, 496, 425, 531, 425, 425, 496, 390, 425, 638, 460, 425, 531, 390, 425.
2.703 g/l,A	every 2mm 425, 354, 461, 319, 354, 390, 354, 567, 531, 531, 425, 425, 567, 496, 531, 461, 425, 496, 354, 461.
2.703 g/l,B	every 2 mm 850, 850, 815, 1028, 673, 815, 638, 709, 673, 496, 425, 496, 461, 496, 638, 319, 425, 496, 390, 354, 496, 354, 425, 354, 319, 425, 283.
3.243 g/l,A	every 2mm 354, 354, 461, 461, 461, 531, 425, 638, 638, 673, 638, 602, 531, 602, 602, 496, 496, 496, 567, 567.
3.243 g/l,B	every 2 mm 957, 1028, 992, 921, 1028, 921, 921, 709, 780, 815, 744, 886, 709, 673, 602, 602, 531, 567, 425, 354, 425, 496, 425, 390, 461, 496, 390, 319.
4.324 g/l,A	every 2 mm 992, 921, 921, 992, 780, 992, 1169, 850, 921, 886, 780, 921, 815, 992, 992, 744, 992, 886, 815, 886.
4.324 g/l,B	every 2 mm 673, 638, 709, 744, 567, 531, 709, 638, 638, 673, 744, 709, 815, 744, 744, 921, 921, 815, 921, 744, 815, 850, 886, 886, 850, 886, 815, 850, 815.

6.486 g/l Chromium deposition, no cracking.

SODIUM FLUORIDE ADDITIONS, GLASS CONTAINER

2.5 g/l,A every 2 mm 20, 20, 0, 20, 20, 0, 20, 0, 20, 20, 20, 20, 20, 20, 20, 20, 20, 20, 0, 0,

2.5 g/l,B every 1 mm 20, 20, 20, 20, 0, 20, 0, 20, 20, 20, 20, 20, 20, 0, 0, 20, 20, 20, 20, 20, 20, 20, 20, 20, 20, 0, 20, 20, 0, 20, 20, 20, 20, 20.
then every 2 mm 39, 39, 39, 39.

3.0 g/l,A every 2 mm 79, 79, 118, 197, 177, 98, 118, 177, 138, 138, 157, 138, 138, 98, 118, 157, 59, 79, 79, 118.

3.0 g/l,A every 1 mm 39, 39, 20, 39, 20, 20, 39, 59, 20, 39, 39, 39, 39, 59, 39, 59, 59, 39, 98, 59, 138, 98, 138, 177, 138, 118, 157, 197, 157, 177, 197, 217, 217, 197, 256, 295, 295, 315, 315, 256, 236, 236, 276, 256, 276, 256, 276, 256, 256, 295, 276, 276, 276, 295, 413, 236, 374.

3.5 g/l,A every 2mm 551, 650, 669, 610, 591, 669, 630, 591, 571, 551, 512, 630, 591, 591, 591, 650, 551, 512, 512, 551.

3.5 g/l,B every 1 mm 39, 39, 39, 79, 98, 177, 157, 256, 315, 295, 374, 315, 413, 394, 413, 453, 512, 492, 453, 571, 551, 650, 531, 512, 591, 591, 689, 728, 650, 669, 630, 689, 689, 689, 748, 669, 787, 787, 906, 886
then every 2 mm 787, 728, 827, 886.

3.75 g/l,A every 2 mm 1181, 1122, 1122, 1122, 1299, 1093, 1181, 1093, 1063, 1063, 1033, 1004, 1063, 1004, 1033, 1122, 1181, 1122, 1122, 1122.

3.75 g/l,B every 1 mm 79, 157, 217, 295, 472, 492, 650, 630, 728, 827, 768, 886, 886, 1063, 965, 1024, 1122, 1240, 1043, 1181.
then every 2 mm 1240, 1181, 1319, 1240, 1181, 1181, 1339.

4.0 g/l	No chromium deposition.

SODIUM FLUOROSILICATE ADDITIONS, PLASTIC CONTAINER

1.304 g/l,A	every 2 mm 0, 24, 24, 47, 24, 24, 24, 0, 24, 24, 0, 24, 47, 24, 0, 0, 0, 0, 24, 24.
1.304 g/l,B	every 2mm 24, 24, 47, 24, 24, 24, 24, 47, 24, 0, 0, 0, 0, 0, 0, 0, 0, 0, 24, 0, 0, 24, 0, 24, 0, 24, 24, 24, 0.
2.608 g/l,A	every 2 mm 71, 71, 71, 47, 24, 71, 71, 47, 71, 71, 47, 71, 47, 24, 47, 24, 47, 47, 0, 71.
2.608 g/l,B	every 2 mm 118, 142, 118, 189, 142, 165, 118, 165, 47, 47, 94, 94, 47, 71, 47, 118, 47, 118, 47, 94, 71, 71, 94, 47, 24, 94, 47, 0, 24, 24.
5.216 g/l,A	every 2 mm 461, 496, 602, 673, 709, 780, 602, 602, 709, 709, 709, 638, 709, 638, 709, 638, 709, 744, 638, 709.
5.216 g/l,B	every 2 mm 815, 1417, 1063, 1098, 1063, 1063, 886, 921, 1134, 921, 1063, 780, 673, 638, 531, 496.
7.824 g/l	Chromium deposition, no cracking.

POTASSIUM FLUORIDE ADDITIONS, GLASS CONTAINER

2.768 g/l	Chromium deposition, no cracking.
3.460 g/l,A	every 2 mm 39, 39, 20, 20, 20, 0, 20, 20, 0, 0, 20, 20, 20, 0, 20, 0, 20, 20, 39, 20.
3.460 g/l,B	every 1 mm 0, 20, 20, 20, 39, 20, 20, 20, 20, 20, 20, 20, 20, 0, 0, 0, 20, 0, 20, 0, 20, 0, 0, 0, 0, 20, 0, 0, 0, 0, 0, 0, 20, 20, 0, 0, 0, 20, 20, 0, 20, 0, 0, 0, 0, 20, 20, 0, 0, 0, 0, 0, 20, 20, 20.
4.152 g/l,A	every 2 mm 39, 20, 39, 39, 39, 20, 59, 20, 39, 59, 39, 59, 39, 20, 39, 59, 59, 39, 39, 39.

4.152 g/1,B every 1 mm 39, 20, 20, 0, 0, 20, 0, 0, 20, 20, 39, 39, 39, 39, 39, 39, 39, 39, 59, 39, 59, 39, 59, 59, 59, 59, 39, 39, 59, 30, 59, 59, 30, 30, 59, 59, 59, 59, 59, 30, 59, 30, 59, 79, 39, 59, 79, 59, 79, 59, 79, 59, 59, 39, 79.

4.844 g/1,A every 2 mm 118, 165, 94, 189, 213, 307, 236, 260, 236, 213, 260, 307, 283, 283, 283, 213, 189, 165, 142, 142.

4.844 g/1,B every 2 mm 47, 0, 71, 71, 118, 94, 94, 142, 142, 189, 283, 236, 260, 307, 236, 283, 260, 260, 331, 331, 331, 307, 283, 283, 207, 354, 402, 449.

5.536 g/1,A every 2 mm 945, 886, 886, 827, 886, 974, 886, 974, 945, 886, 886, 915, 945, 945, 974, 827, 886, 886, 827, 827.

5.536 g/1,B every 1 mm 256, 276, 256, 236, 256, 256, 354, 433, 453, 453, 492, 531, 531, 630, 669, 827, 846, 856, 846, 787.
then every 2 mm 886, 945, 1004, 1043.
every 2 mm Lo63, 1063, 1063, 1181, 1181, 1181, 1201, 1319, 1476, 1319, 1319, 1476, 1476, 1476.

6.228 g/1,A Difficult to count, estimate 1181.

6.228 g/1,B every 1 mm 39, 118, 236, 295, 374, 512, 591, 709, 709, 768, 768, 886, 1043, 1122.
every 1 mm 1240, 1063, 1102, 1102, 1181, 1299, 1299, 1299.

6.920 g/1,A Difficult to count, estimate 984.

6.920 g/1,B every 1 mm 20, 20, 59, 236, 453, 433, 472, 650, 709, 669, 787,
then difficult to count estimate 709.

7.6112 g/1 No chromium deposition.

POTASSIUM FLUOROSILICATE ADDITIONS, GLASS CONTAINER

1.529 g/1	Chromium deposition, no cracking.
3.058 g/1,A	every 2 mm 390, 319, 213, 354, 213, 283, 248, 319, 319, 213, 319, 390, 425, 213, 213, 248, 248, 248, 319, 354.
3.058 g/1,B	every 2 mm 390, 461, 567, 638, 638, 425, 390, 390, 283, 390, 319, 248, 319, 283, 290, 354, 283, 248, 213, 283, 354, 354, 248, 319, 283, 248, 283, 248.
6.116 g/1,A	every 4 mm 709, 744, 709, 638, 602, 638, 709, 673, 567, 673, 780, 709, 709.
6.116 g/1,B	every 2 mm 886, 1205, 992, 780, 673, 815, 780, 709. then every 4 mm 673, 673, 744, 709, 709, 780, 815, 780.
9.174 g/1,A	every 2 mm 709, 780, then every 4 mm 709, 638, 709, 638, 709, 709, 673, 709, 709, 709, 709.
9.174 g/1,B	every 2 mm 886, 992, 1063, 992, 1063. then every 4 mm 815, 850, 1063, 815, 709, 886, 709, 638. estimate of 5 more counts 709.
12.232 g/1	Chromium deposition, no cracking.

RUBIDIUM FLUORIDE ADDITIONS, GLASS CONTAINER

1.333 g/1	Chromium deposition, no cracking.
2.666 g/1	Chromium deposition, no cracking.
6. 666 g/1,A	every 1 mm 118, 98, 197, 157, 177, 98, 98, 118, 79, 118, 217, 177, 138, 157, 79, 118, 177, 177, 197, 177, 98, 157, 197, 197, 98, 98, 177, 138, 138, 177, 98, 79, 79, 98, 79, 79, 79, 98, 138, 98.

6.666 g/l,B	every 1 mm 20, 39, 39, 59, 118, 39, 39, 118, 98, 118, 59, 98, 138, 118, 79, 138, 98, 118, 118, 79, 197, 79, 59, 79, 79, 79, 177, 118, 79, 157, 217, 236, 177, 197, 236, 217, 197, 197, 236, 197, 157, 177, 177, 177, 157, 256, 256, 236, 335, 256, 217, 295, 276, 315, 295.

CAESIUM FLUORIDE ADDITIONS, GLASS CONTAINER

1.809 g/l	Chromium deposition, no cracking.
4.037 g/l,A	every 2 mm 20, 0, 20, 20, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 20, 0, 0, 20,
4.037 g/l,B	every 1 mm 0, 20, 0, 0, 20, 20, 20, 0, 0, 20, 20, 20, 0, 20, 20, 20, 0, 20, 0, 20, 20, 20, 20, 20, 20, 20, 20, 20, 20, 0, 0, 20, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 20, 0, 20, 20, 0, 20, 0, 0, 0, 0, 0, 0, 20, 0.
5.647 g/l,A	every 2 mm 39, 39, 20, 20, 20, 39, 20, 39, 20, 59, 39, 20, 39, 20, 39, 39, 20, 59, 59, 39.
5.647 g/l,B	every 1 mm 0, 0, 20, 0, 0, 0, 20, 0, 20, 0, 0, 0, 0, 0, 0, 0, 20, 20, 0, 0, 20, 0, 20, 20, 0, 20, 39, 20, 20, 20, 0, 20, 39, 39, 20, 59, 59, 20, 59, 59, 39, 0, 20, 39, 59, 39, 20, 39, 39, 20, 79.
7.234 g/l,A	every 2 mm 531, 413, 502, 472, 591, 531, 531, 413, 502, 531, 620, 472, 443, 443, 472, 511, 591.
7.234 g/l,B	every 1 mm 79, 98, 157, 157, 217, 236, 295, 276, 374, 276, 335, 335, 295, 374, 295, 453, 335, 354, 394, 433, 433, 551, 413, 413, 531, 433, 472, 472, 531, 551, 512, 492, 512, 531, 492, 689, 610, 591, every 1 mm 591, 591, 591, 591, 728, 650, 750, 709, 650, 669, 669, 591.
8.813 g/l,A	Difficult to count, estimated 1181.

8.813 g/1,B	every 1 mm 394, 256, 512, 531, 551, 650, 728, 787, 787, 827, 886, 886, 945, 1024, 1063, 1024, 1024, 1181. then difficult to count, estimated 1181.

CAESIUM FLUOROSILICATE ADDITIONS, GLASS CONTAINER

2.831 g/1,A	every 2 mm 0, 35, 0, 0, 35, 0, 0, 35, 35, 0, 0, 35, 35, 35, 0, 35, 0, 0, 0, 0,
2.831 g/1,B	every 2 mm 35, 35, 35, 0, 0, 0, 0, 35, 0, 0, 35, 0, 0, 71, 35, 0, 0, 0, 0, 0, 0, 0, 35, 0, 0, 35, 0, 35, 35, 0, 0.
5.662 g/1,A	every 2 mm 213, 213, 390, 213, 213, 354, 283, 354, 319, 248, 319, 283, 425, 142, 354, 425, 283, 213, 319, 283.
5.662 g/1,B	every 2 mm 496, 531, 709, 709, 744, 744, 744, 496, 248, 248, 319, 354, 283, 248, 248, 248, 177, 283, 248, 248, 283, 213, 248.
7.520 g/1,A	every 2 mm 319, 283, 213, 354, 354, 425, 425, 354, 461, 425, 496, 496, 496, 390, 496, 354, 425, 496, 248, 319.
7.520 g/1,B	every 2 mm 531, 850, 1028, 921, 992, 850, 780, 780, 638, 567, 425, 602, 531, 461. every 2 mm 390, 390, 390, 390, 354, 425, 425, 319, 390, 319, 390, 354, 354, 319.
11.324 g/1,A	every 2 mm 236, 165, 165, 189, 142, 165, 165, 94, 165, 189, 189, 118, 94, 165, 118, 213, 213, 189, 189, 189.
11.324 g/1,A	every 2 mm 142, 142, 94, 197, 71, 94, 94, 71, 165, 142, 118, 142, 142, 165, 118, 118, 213, 165, 94, 94, 165, 165, 142, 118, 213, 189, 189.

AMMONIUM FLUORIDE ADDITIONS, GLASS CONTAINER

1.762 g/1	About 10 cracks only.

2.205 g/1,A	every 1 mm 20, 20, 20, 20, 20, 20, 20, 0, 0, 20, 20, 20, 20, 20, 20, 20, 20, 39, 39, 39, 20, 39, 20, 39, 20, 20, 20, 0, 20, 0, 20, 20, 20, 20, 39, 39, 39, 39, 20, 20.
2.205 g/1,B	every 1 mm 0, 0, 20, 20, 20, 20, 20, 20, 39, 39, 20, 20, 20, 0, 0, 0, 20, 0, 0, 0, 20, 20, 20, 20, 0, 20, 39, 20, 0, 0, 20, 20, 20, 39, 20, 20, 20, 20, 39, 20, 39, 39, 39, 39, 20, 39, 39, 20, 20, 20, 39, 39, 39, 39.
2.646 g/1,A	every 1 mm 118, 59, 79, 39, 59, 59, 79, 79, 59, 39, 39, 39, 39, 39, 39, 39, 79, 39, 39, 39, 39, 39, 39, 39, 59, 39, 39, 118, 79, 98, 39, 39, 39, 39, 39, 59, 79, 59, 118, 98, 79, 118,
2. 646 g/1,B	every 1 mm 0, 0, 39, 39, 39, 20, 39, 39, 20, 20, 59, 39, 39, 39, 59, 39, 39, 59, 20, 39, 20, 20, 39, 39, 79, 39, 79, 39, 39, 39, 79, 59, 59, 39, 79, 59, 59, 98, 59, 59, 59, 79, 39, 79, 98, 79, 98, 98, 59, 98.
3.087 g/1,A	every 1 mm 197, 138, 118, 177, 157, 118, 118, 177, 177, 118, 118, 118, 157, 177, 138, 157, 177, 118, 177, 138, 177, 197, 138, 138, 138, 197, 177, 138, 177, 197, 197, 157, 118, 177, 197, 177, 157, 157, 157, 177.
3.087 g/1,B	every 1 mm 20, 39, 20, 39, 39, 98, 59, 157, 59, 79, 118, 59, 79, 39, 138, 118, 98, 118, 118, 118, 138, 177, 157, 177, 118, 177, 197, 157, 197, 197, 197, 177, 157, 256, 217, 177, 217, 217, 236, 217, 236, 236, 256, 295, 276, 256, 256, 354, 276, 315, 354, 413, 413, 453, 472.
3.528 g/1,A	every 1 mm 256, 276, 276, 295, 335, 315, 413, 472, 492, 531, 472, 551, 709, 531, 571, 610, 591, 610, 551, 531, 630, 669, 591, 630, 709, 630, 551, 669, 551, 650, 630, 650, 630, 571, 610, 689, 669, 709, 591, 551.
3.528 g/1,A	every 1 mm 39, 98, 157, 118, 236, 276, 197, 236, 295, 256, 394, 394, 413, 433, 433, 394, 492, 412, 433, 443, 650, 650, 591, 709, 738, 797, 709, 709, 650, 738, 709, 797, 797, 709, 738, 768, 738, 709, 856.

	every 1 mm 856, 945, 886, 915, 886, 886, 856, 709, 886, 945, 945, 945, 945, 856, 974, 886, 1004, 768, 974, 886, 886, 886.
4.410 g/1	No chromium deposition.
5.292 g/1	No chromium depositon.

AMMONIUM FLUOROSILICATE ADDITIONS, PLASTIC CONTAINER

1.236 g/1,A	every 2 mm 24, 24, 47, 24, 47, 47, 0, 24, 94, 94, 47, 24, 0, 47, 24, 24, 47, 47, 0, 0.
1.236 g/1,B	every 2 mm 71, 47, 94, 71, 71, 71, 24, 24, 24, 47, 71, 47, 0, 24, 71, 71, 24, 24, 0, 71, 47, 47, 24, 71, 24, 24, 47, 24.
2.472 g/1,A	every 2 mm 142, 142, 106, 106, 106, 106, 142, 213, 213, 177, 213, 213, 71, 177, 142, 177, 142, 106, 106, 142.
2.472 g/1,B	every 2 mm 591, 638, 531, 390, 213, 283, 319, 177, 177, 142, 177, 213, 142, 213, 106, 106, 213, 71, 142, 142, 177, 177, 142, 142, 71.
3.708 g/1,A	every 2 mm 425, 425, 248, 354, 354, 354, 283, 354, 354, 354, 213, 354, 425, 496, 425, 354, 425, 354, 319, 496.
3.708 g/1,B	every 2 mm 957, 780, 850, 780, 850, 744, 602, 496, 354, 319, 390, 425, 354. every 2 mm 283, 283, 354, 354, 319, 319, 283, 319, 213, 354, 319.
4.944 g/1,A	every 2 mm 709, 815, 744, 780, 850, 886, 744, 850, 780, 815, 815, 744, 780, 780, 850, 815, 850.
4.944 g/1,B	every 1 mm 744, 602. every 2 mm 567, 638, 673, 709, 638, 638, 709, 744, 780, 638, 780, 709, 709, 780, 850, 886, 850, 850, 780, 815, 815, 850, 815, 921.

7.416 g/l	Chromium deposition, no cracking.

HYDROFLUOSILICIC ACID ADDITIONS, PLASTIC CONTAINER

0.5 g/l	Chromium deposition, no cracking.
1.0 g/l,A	every 1 mm 24, 0, 0, 0, 0, 24, 0, 24, 0, 0, 47, 0, 24, 0, 0, 24, 47, 24, 0, 0, 24, 24, 0, 0, 0, 47, 47, 24, 0, 0, 0, 0, 0, 0, 24, 24, 0, 0, 0, 0.
1.0 g/l,B	every 1 mm 47, 0, 71, 24, 24, 0, 47, 24, 24, 0, 24, 71, 47, 0, 47, 71, 47, 47, 47, 47, 47, 47, 47, 47, 0, 0, 0, 47, 0, 0, 47, 47, 0, 0, 0, 0, 0, 0, 0, 0, 24, 47, 0, 24, 47, 47, 24, 47, 0, 0, 47, 24, 0, 0, 0, 0, 0, 0, 0, 24.
2.0 g/l,A	every 2 mm 744, 673, 673, 709, 673, 744, 815, 815, 744, 850, 780, 709, 850, 673, 780, 673, 638, 744, 709, 744.
2.0 g/l,B	every 1 mm 591, 520, 661, 567, 756, 685, 591, 709, 756, 756, 843, 843, 661, 661, 756, 614, 756, 732, 866, 756, 567, 567, 661, 614, 732, 661, 685, 661, 638, 661, 685, 614, 614, 661, 638, 638, 614, 543, 591, 520, 638, 614, 449, 520, 543, 520, 520, 449, 520, 496, 472.
3.0 g/l,A	Difficult to count, estimate 850
3.0 g/l,B	Difficult to count, estimate 850
4.0 g/l,A	Difficult to count, estimate 1063
4.0 g/l,B	Difficult to count estimate 1063
5.0 g/l	Chromium deposition, no cracking.

EFFECT OF CONTAINER ON THE FLUORIDE CATALYST

All counts taken in position A.

4.844 g/l potassium fluoride.

Plating time minutes	Container	Crack count
50	Plastic	Chromium deposition, no cracking
145	Plastic	Chromium deposition, no cracking
195	Plastic	Chromium deposition, no cracking
235	Glass	0, 0, 24, 47, 71, 24, 0, 24, 71, 47, 24, 71, 24, 47, 0, 47, 71, 24, 24, 47
295	Plastic	24, 47, 24, 24, 0, 0, 47, 47, 0, 24, 47, 47, 71, 71, 71, 24, 71, 71, 71, 0
50	Glass	118,165, 94, 189, 213, 307, 236, 260, 236, 213, 260, 307, 283, 283, 283, 213, 189, 165, 142, 142
160	Glass	213, 213, 260, 213, 213, 246, 283, 189, 307, 213, 283, 189, 260, 307, 213, 236, 142, 142, 189, 213
250	Glass	260, 283, 213, 213, 260, 260, 189, 236, 213, 331, 213, 189, 213, 236, 213, 213, 260, 213, 189, 189
370	Glass	165, 236, 260, 189, 142, 165, 260, 189, 165, 189, 213, 189, 118, 142, 283, 213, 189, 189, 213, 213
460	Glass	118, 71, 71, 71, 94, 94, 118, 142, 94, 71, 118, 118, 47, 47, 94, 47, 71, 94, 47, 47
550	Glass	94, 94, 165, 118, 142, 94, 94, 94, 47, 118, 71, 47, 71, 71, 71, 71, 71, 118, 71, 94

Plating time minutes	Container	Crack count
595	Glass	496, 461, 461, 567, 496, 461, 390, 390, 425, 531, 461, 461, 390, 425, 390, 531, 531, 531, 425, 496
645	Glass	638, 602, 461, 531, 602, 531, 567, 496, 390, 461, 390, 461, 390, 425, 390, 390, 354, 390, 425, 425
50	Glass	118, 165, 94, 189, 213, 307, 236, 260, 236, 213, 260, 307, 283, 283, 283, 213, 189, 165, 142, 142
175	Plastic	165, 165, 189, 142, 165, 118, 236, 165, 213, 165, 213, 213, 189, 213, 165, 213, 189, 189, 165, 189
340	Plastic	118, 94, 118, 47, 47, 71, 47, 94, 71, 71, 47, 94, 0, 24, 71, 94, 71, 47, 71, 94
430	Plastic	71, 94, 47, 47, 47, 0, 0, 0, 24, 24, 0, 0, 47, 0, 0, 47, 47, 71, 71, 71
540	Plastic	47, 47, 47, 47, 47, 47, 47, 0, 24, 0, 0, 0, 24, 47, 47, 24, 47, 24, 71, 71
590	Plastic	661, 661, 638, 685, 638, 520, 591, 567, 614, 709, 543, 543, 520, 472, 520, 638, 638, 520, 614, 685
650	Plastic	No chromium deposition.

2.0 g/l hydrofluosilicic acid

Plating time minutes	Container	Crack count
50	Glass	709, 673, 709, 531, 602, 567, 531, 496, 602, 461, 496, 425, 567, 425, 602, 531, 531, 425, 638, 567
200	Glass	638, 567, 709, 673, 638, 567, 496, 461, 496, 496, 531, 531, 461, 461, 531, 531, 638, 531, 531, 567
325	Glass	531, 638, 496, 461, 354, 213, 319, 283, 283, 213, 142, 248, 213, 177, 213, 248, 213, 213, 319, 319

Leave without plating 1020 minutes

Plating time minutes	Container	Crack count
420	Glass	886, 780, 850, 850, 921, 850, 780, 992, 850, 886, 744, 780, 886, 921, 886, 886, 886, 850, 921, 780
50	Plastic	744, 673, 673, 744, 673, 744, 815, 815, 744, 850, 780, 709, 850, 673, 780, 673, 638, 744, 709, 744
260	Plastic	390, 390, 461, 461, 531, 567, 673, 638, 496, 602, 531, 531, 531, 673, 531, 496, 390, 425, 425, 425
455	Plastic	390, 390, 319, 425, 496, 496, 567, 390, 531, 425, 531, 425, 425, 461, 390, 425, 319, 390, 354, 461
560	Plastic	177, 177, 248, 248, 283, 283, 425, 354, 461, 390, 390, 354, 461, 354, 354, 461, 390, 283, 283, 177

Plating time minutes	Container	Crack count
610	Plastic	921, 921, 815, 921, 886, 815, 1098, 1063, 1240, 1098, 1240, 1063, 1063, 1240, 957, 886, 1240, 992, 1205, 1098

EFFECT OF REDUCED CHROMIUM

4.844 g/l potassium fluoride, glass container

Calculated Cr^{+++} g/l	Crack count
0.0	118, 165, 94, 189, 213, 307, 236, 260, 236, 213, 260, 307, 283, 283, 283, 213, 189, 165, 142, 142
0.3	142, 142, 71, 118, 213, 118, 118, 142, 142, 236, 213, 213, 213, 213, 142, 189, 213, 213, 236, 165
1.0	118, 165, 142, 142, 142, 118, 189, 142, 165, 165, 165, 165, 213, 189, 189, 189, 189, 165, 213, 165
2.0	142, 142, 118, 189, 165, 189, 283, 236, 189, 165, 189, 189, 236, 213, 213, 260, 94, 213, 142, 118
4.0	236, 260, 331, 354, 213, 354, 260, 236, 307, 283, 283, 236, 307, 331, 189, 378, 165, 189, 283, 189
6.0	189, 213, 236, 236, 260, 283, 307, 213, 354, 307, 354, 283, 307, 283, 283, 236, 283, 283, 283, 283

COMPARISON OF CURRENT SUPPLY

4.844 g/l potassium fluoride, glass container

Battery current supply	189, 283, 189, 189, 189, 189, 283, 283, 213, 260, 307, 331, 283, 354, 260, 236, 283, 260, 236, 236

2.0 g/l hydrofluosilicic acid, plastic container

Battery current supply 709, 709, 567, 602, 461, 709, 531, 673, 709, 567, 602, 602, 496, 638, 602, 602, 567, 638, 709, 638

HULL CELL RESULTS

Covering Power

Lithium Fluoride Additions

LiF g/l	F g/l	Current density of initial chromium deposition A/dm^2
0.309	0.226	2.47(3)
0.618	0.452	1.93(5)
0.927	0.679	3.97(8)
1.237	0.906	6.23(5)
1.854	1.358	9.67(5)
2.471	1.810	14.43(8)
2.780	2.036	17.20(0)

Sodium fluoride additions

NaF g/l	F g/l	Current density of initial chromium deposition A/dm^2
0.500	0.226	1.93(5)
1.000	0.452	2.47(3)
1.500	0.679	4.51(5)
2.000	0.906	7.52(5)
2.500	1.131	9.13(8)
3.000	1.358	10.96(5)
3.500	1.584	11.82(5)
3.750	1.697	14.51(3)
4.000	1.810	15.58(8)

Potassium fluoride additions

KF g/1	F g/1	Current density of initial chromium deposition A/dm^2
0.692	0.226	2.36(5)
1.384	0.452	1.93(5)
2.076	0.679	3.44(0)
2.768	0.906	6.77(3)
3.460	1.131	9.13(8)
4.125	1.358	11.28(8)
4.844	1.584	12.90(0)
5.536	1.810	14.51(3)
6.228	2.036	18.81(3)

Rubidium fluoride additions

RbF g/1	F g/1	Current density of initial chromium deposition A/dm^2
1.333	0.242	1.93(5)
2.666	0.484	2.68(8)
6.666	1.212	11.82(5)

Caesium fluoride additions

CsF g/1	F g/1	Current density of initial chromium deposition A/dm^2
1.809	0.226	2.04(3)
4.037	0.505	7.52(5)
5.647	0.706	9.67(5)
7.234	0.906	15.58(8)

Ammonium fluoride additions

NH_4F g/l	F g/l	Current density of initial chromium deposition A/dm^2
0.441	0.226	1.93(5)
0.882	0.452	3.01(0)
1.323	0.679	7.52(5)
1.762	0.906	10.75(0)
2.205	1.131	9.13(8)
2.646	1.358	15.05(0)
3.087	1.584	21.50(0)
3.528	1.810	20.42(5)

Lithium fluorosilicate additions

Li_2SiF_6 g/l	F g/l	Current density of initial chromium deposition A/dm^2
1.081	0.790	3.54(8)
1.622	1.186	3.76(3)
2.162	1.580	6.98(8)
2.703	1.976	8.60(0)
3.243	2.372	11.82(5)
4.324	3.160	13.43(8)
6.486	4.740	21.50(0)

Sodium fluorosilicate additions

Na_2SiF_6 g/l	F g/l	Current density of initial chromium deposition A/dm^2
1.304	0.790	2.68(8)
2.608	1.580	7.52(5)
5.216	3.160	11.28(8)
7.824	4.740	20.96(3)

Potassium fluorosilicate additions

K_2SiF_6 g/l	F g/l	Current density of initial chromium deposition A/dm^2
1.529	0.790	4.83(8)
3.058	1.580	8.60(0)
6.116	3.160	11.82(5)
9.174	4.740	17.200

Caesium fluorosilicate additions

Cs_2SiF_6 g/1	F g/1	Current density of initial chromium deposition A/dm^2
2.831	0.790	4.83(8)
5.662	1.580	9.67(5)
7.520	2.102	13.97(5)
11.324	3.160	21.50(0)

Ammonium fluorosilicate additions

$(NH_4)_2SiF_6$ g/1	F g/1	Current density of initial chromium deposition A/dm^2
1.236	0.790	4.83(8)
2.472	1.580	7.52(5)
3.708	2.372	11.28(8)
4.944	3.160	13.43(8)
7.416	4.740	19.35(0)

Hydrofluosilicic acid additions

H_2SiF_6 g/1	F g/1	Current density of initial chromium deposition A/dm^2
0.500	0.395	2.15(0)
1.000	0.790	5.91(3)
2.000	1.580	8.06(3)
3.000	2.372	11.28(8)
4.000	3.160	16.66(3)

CRACKS COUNTS, CURRENT DENSITY, FLUORIDE CONCENTRATION, FOR MULTIPLE REGRESSION ANALYSIS

LiF g/1	F g/1	Current density A/dm^2	Crack counts cracks/10 mm
0.309	0.226	51.7	98
0.309	0.226	39.2	20
0.618	0.452	51.7	59
0.618	0.452	39.2	39
0.618	0.452	33.4	20
0.927	0.679	51.7	39
0.927	0.679	39.2	59
0.927	0.679	33.4	39
0.927	0.679	29.6	20
0.927	0.679	26.7	20
1.237	0.906	51.7	98
1.237	0.906	39.2	59

Lif g/1	F g/1	Current density A/dm^2	Crack counts cracks/10 mm
1.237	0.906	33.4	39
1.237	0.906	29.6	59
1.237	0.906	26.7	59
1.237	0.906	24.4	20
1.237	0.906	22.5	20
1.237	0.906	20.9	20
1.237	0.906	19.5	20
1.854	1.358	51.7	236
1.854	1.358	39.2	118
1.854	1.358	33.4	118
1.854	1.358	29.6	59
1.854	1.358	26.7	79
1.854	1.358	24.4	39
1.854	1.358	22.5	20
1.854	1.358	20.9	39
1.854	1.358	19.5	20
2.471	1.810	51.7	354
2.471	1.810	43.8	295
2.471	1.810	39.2	217
2.471	1.810	35.9	335
2.471	1.810	33.4	335
2.471	1.810	31.3	315
2.471	1.810	29.6	335
2.471	1.810	28.0	394
2.471	1.810	26.7	492
2.780	2.036	51.7	158
2.780	2.036	43.8	98
2.780	2.036	39.2	138
2.780	2.036	35.9	217
2.780	2.036	33.4	295
2.780	2.036	31.3	315
2.780	2.036	29.6	256
2.780	2.036	28.0	276
2.780	2.036	26.7	236

Sodium fluoride additions

NaF g/1	F g/1	Current density A/dm^2	Crack counts cracks/10 mm
0.500	0.226	51.7	59
0.500	0.226	39.2	39
0.500	0.226	33.4	20
0.500	0.226	29.6	20
1.000	0.452	51.7	39
1.000	0.452	39.2	39
1.000	0.452	33.4	20
1.000	0.452	29.6	20
1.500	0.679	51.7	39
1.500	0.679	39.2	39
1.500	0.679	33.4	20
1.500	0.679	29.6	20
1.500	0.679	26.7	20

NaF g/1	F g/1	Current density A/dm^2	Crack counts cracks/10 mm
1.500	0.679	24.4	20
2.000	0.906	51.7	39
2.000	0.906	39.2	39
2.000	0.906	33.4	39
2.000	0.906	31.3	39
2.000	0.906	29.6	39
2.000	0.906	26.7	20
2.000	0.906	24.4	20
2.000	0.906	22.5	20
2.000	0.906	20.9	20
2.000	0.906	19.5	20
2.500	1.131	51.7	98
2.500	1.131	39.2	39
2.500	1.131	33.4	59
2.500	1.131	29.6	59
2.500	1.131	26.7	39
2.500	1.131	24.4	39
2.500	1.131	22.5	39
2.500	1.131	20.9	39
2.500	1.131	19.5	39
2.500	1.131	18.2	20
2.500	1.131	17.1	20
2.500	1.131	16.0	39
2.500	1.131	15.1	39
2.500	1.131	14.2	20
2.500	1.131	13.4	20
3.000	1.358	51.7	177
3.000	1.358	39.2	157
3.000	1.358	33.4	79
3.000	1.358	29.6	59
3.000	1.358	26.7	79
3.000	1.358	24.4	59
3.000	1.358	22.5	59
3.000	1.358	20.9	79
3.000	1.358	19.5	59
3.000	1.358	18.2	79
3.000	1.358	17.1	59
3.000	1.358	16.0	59
3.000	1.358	15.1	98
3.000	1.358	14.2	295
3.000	1.358	13.4	394
3.000	1.358	12.6	79
3.000	1.358	11.9	236
3.500	1.584	51.7	177
3.500	1.584	39.2	138
3.500	1.584	33.4	118
3.500	1.584	29.6	98
3.500	1.584	26.7	98
3.500	1.584	24.4	74
3.500	1.584	22.5	118
3.500	1.584	20.9	157
3.500	1.584	19.5	157
3.500	1.584	18.2	157
3.500	1.584	17.1	157

NaF g/1	F g/1	Current density A/dm^2	Crack counts cracks/10 mm
3.500	1.584	16.0	98
3.500	1.584	15.1	256
3.750	1.697	51.7	39
3.750	1.697	39.2	59
3.750	1.697	33.4	98
3.750	1.697	29.6	79
3.750	1.697	26.7	59
3.750	1.697	24.4	59
3.750	1.697	22.5	118
3.750	1.697	20.9	118
3.750	1.697	19.5	138
3.750	1.697	18.2	177
4.000	1.810	51.7	157
4.000	1.810	39.2	177
4.000	1.810	33.4	177
4.000	1.810	29.6	236
4.000	1.810	26.7	276
4.000	1.810	24.4	256
4.000	1.810	22.5	295
4.000	1.810	20.9	276

Potassium fluoride additions

KF g/1	F g/1	Current density A/dm^2	Crack counts cracks/10 mm
0.692	0.226	51.7	59
0.692	0.226	39.2	39
0.692	0.226	33.4	39
1.384	0.452	51.7	59
1.384	0.452	39.2	39
1.384	0.452	33.4	20
1.384	0.452	29.6	20
2.076	0.679	51.7	59
2.076	0.679	39.2	39
2.076	0.679	33.4	39
2.076	0.679	29.6	20
2.076	0.679	26.7	20
2.076	0.679	24.4	20
2.076	0.679	22.5	20
2.076	0.679	20.9	20
2.768	0.906	51.7	39
2.768	0.906	39.2	39
2.768	0.906	33.4	20
2.768	0.906	29.6	20
2.768	0.906	26.7	20
2.768	0.906	24.4	20
2.768	0.906	22.5	20
2.768	0.906	20.9	20
2.768	0.906	19.5	20
3.460	1.131	51.7	59
3.460	1.131	39.2	59

KF g/l	F g/l	Current density A/dm^2	Crack counts cracks/10 mm
3.460	1.131	33.4	59
3.460	1.131	29.6	39
3.460	1.131	26.7	39
3.460	1.131	24.4	39
3.460	1.131	22.5	59
3.460	1.131	20.9	20
3.460	1.131	19.5	59
3.460	1.131	18.2	20
3.460	1.131	17.1	20
3.460	1.131	16.0	20
4.125	1.358	51.7	59
4.125	1.358	39.2	59
4.125	1.358	33.4	98
4.125	1.358	29.6	79
4.125	1.358	26.7	59
4.125	1.358	24.4	59
4.125	1.358	22.5	39
4.125	1.358	20.9	39
4.125	1.358	19.5	39
4.125	1.358	18.2	39
4.125	1.358	17.1	39
4.125	1.358	16.0	20
4.125	1.358	15.1	20
4.125	1.358	14.2	79
4.125	1.358	13.4	197
4.125	1.358	12.6	197
4.844	1.584	51.7	177
4.844	1.584	39.2	118
4.844	1.584	33.4	79
4.844	1.584	29.6	98
4.844	1.584	26.7	98
4.844	1.584	24.4	79
4.844	1.584	22.5	59
4.844	1.584	20.9	157
4.844	1.584	19.5	79
4.844	1.584	18.2	98
4.844	1.584	17.6	118
4.844	1.584	16.5	157
4.844	1.584	15.5	217
4.844	1.584	14.6	315
5.536	1.810	51.7	98
5.536	1.810	39.2	138
5.536	1.810	33.4	177
5.536	1.810	29.6	118
5.536	1.810	26.7	197
5.536	1.810	24.4	197
5.536	1.810	22.5	177
5.536	1.810	20.9	177
5.536	1.810	19.5	177
5.536	1.810	18.2	216
5.536	1.810	17.1	197

Rubidium fluoride additions

RbF g/l	F g/l	Current density A/dm^2	Crack counts cracks/10 mm
1.333	0.242	51.7	47
1.333	0.242	43.8	24
1.333	0.242	39.2	24
2.666	0.485	51.7	95
2.666	0.485	43.8	24
2.666	0.485	39.2	24
2.666	0.485	35.9	24
2.666	0.485	33.4	24
2.666	0.485	31.3	47
2.666	0.485	29.6	24
2.666	0.485	28.0	24
2.666	0.485	26.7	24
2.666	0.485	25.5	47
2.666	0.485	24.4	24
2.666	0.485	23.4	24
6.666	1.212	51.7	165
6.666	1.212	43.8	118
6.666	1.212	39.2	118
6.666	1.212	35.9	47
6.666	1.212	33.4	95
6.666	1.212	31.3	47
6.666	1.212	29.6	47
6.666	1.212	28.0	47
6.666	1.212	26.7	47
6.666	1.212	25.5	47
6.666	1.212	24.4	71
6.666	1.212	23.4	147
6.666	1.212	22.5	24
6.666	1.212	21.7	47
6.666	1.212	20.9	24
6.666	1.212	20.2	47
6.666	1.212	19.5	24
6.666	1.212	18.8	24
6.666	1.212	18.2	24
6.666	1.212	17.6	24
6.666	1.212	17.1	24

Caesium fluoride additions

CsF g/l	F g/l	Current density A/dm^2	Crack counts cracks/10 mm
1.809	0.226	51.7	79
1.809	0.226	39.2	39
1.809	0.226	33.4	39
1.809	0.226	29.6	20
1.809	0.226	26.7	20
1.809	0.226	24.4	20
1.809	0.226	22.5	20

CsF g/1	F g/1	Current density A/dm^2	Crack counts cracks/10 mm
4.037	0.505	51.7	59
4.037	0.505	39.2	39
4.037	0.505	33.4	59
4.037	0.505	31.3	59
4.037	0.505	29.6	39
4.037	0.505	26.7	20
4.037	0.505	24.4	39
4.037	0.505	22.5	39
4.037	0.505	20.9	39
4.037	0.505	19.5	20
4.037	0.505	18.2	39
4.037	0.505	17.1	20
4.037	0.505	16.0	20
5.647	0.706	51.7	157
5.647	0.706	39.2	98
5.647	0.706	33.4	39
5.647	0.706	29.6	39
5.647	0.706	26.7	39
5.647	0.706	24.4	39
5.647	0.706	22.5	39
5.647	0.706	20.9	39
5.647	0.706	19.5	39
5.647	0.706	18.2	39
5.647	0.706	17.1	39
5.647	0.706	16.0	20
5.647	0.706	15.5	20
5.647	0.706	14.2	39
5.647	0.706	13.4	39
5.647	0.706	12.6	39
5.647	0.706	11.9	39
7.234	0.906	51.7	138
7.234	0.906	39.2	177
7.234	0.906	33.4	118
7.234	0.906	29.6	118
7.234	0.906	26.7	79
7.234	0.906	24.4	118
7.234	0.906	22.5	59
7.234	0.906	20.9	79
7.234	0.906	19.5	118
7.234	0.906	18.2	197
8.813	1.102	51.7	39
8.813	1.102	39.2	39
8.813	1.102	33.4	39
8.813	1.102	29.6	39
8.813	1.102	26.7	39

Ammonium fluoride additions

NH_4F g/1	F g/1	Current density A/dm^2	Crack counts cracks/10 mm
0.441	0.226	51.7	24
0.882	0.452	51.7	71
0.882	0.452	43.8	47
0.882	0.452	39.2	24
0.882	0.452	35.9	24
0.882	0.452	33.4	24
0.882	0.452	31.3	47
0.882	0.452	29.6	24
1.323	0.679	51.7	24
1.323	0.679	43.8	24
1.323	0.679	39.2	24
1.323	0.679	35.9	24
1.323	0.679	33.4	24
1.323	0.679	31.3	24
1.323	0.679	29.6	24
1.762	0.906	51.7	71
1.762	0.906	43.8	47
1.762	0.906	39.2	47
1.762	0.906	35.9	24
1.762	0.906	33.4	47
1.762	0.906	31.3	24
1.762	0.906	29.6	24
1.762	0.906	28.0	24
1.762	0.906	26.7	47
1.762	0.906	25.5	24
1.762	0.906	24.4	24
1.762	0.906	23.4	24
1.762	0.906	22.5	47
2.205	1.131	51.7	95
2.205	1.131	43.8	47
2.205	1.131	39.2	47
2.205	1.131	35.9	95
2.205	1.131	33.4	71
2.205	1.131	31.3	47
2.205	1.131	29.6	47
2.205	1.131	28.0	71
2.205	1.131	26.7	71
2.205	1.131	25.5	47
2.205	1.131	24.4	24
2.205	1.131	23.4	24
2.205	1.131	22.5	47
2.205	1.131	21.7	24
2.205	1.131	20.9	24
2.205	1.131	20.2	47
2.205	1.131	19.5	24
2.205	1.131	18.8	24
2.205	1.131	18.2	24
2.646	1.358	51.7	47
2.646	1.358	43.8	47
2.646	1.358	39.2	24
2.646	1.358	35.9	47

NH_4F g/l	F g/l	Current density A/dm^2	Crack counts cracks/10 mm
2.646	1.358	33.4	47
2.646	1.358	31.3	47
2.646	1.358	29.6	47
2.646	1.358	28.0	47
2.646	1.358	26.7	47
2.646	1.358	25.5	24
2.646	1.358	24.4	24
2.646	1.358	23.4	24
2.646	1.358	22.5	24
3.528	1.810	51.7	24
3.528	1.810	43.8	24
3.528	1.810	39.2	24
3.528	1.810	35.9	47
3.528	1.810	33.4	24
3.528	1.810	31.3	24

Lithium fluorosilicate additions

Li_2SiF_6 g/l	F g/l	Current density A/dm^2	Crack counts cracks/10 mm
1.081	0.790	51.7	118
1.081	0.790	43.8	213
1.081	0.790	39.2	94
1.081	0.790	35.9	24
1.081	0.790	33.4	71
1.081	0.790	31.3	71
1.081	0.790	29.6	24
1.081	0.790	28.0	24
1.081	0.790	26.7	0
1.081	0.790	25.5	0
1.081	0.790	24.4	0
1.081	0.790	23.4	0
1.081	0.790	22.5	0
1.081	0.790	21.7	24
1.081	0.790	20.9	24
1.081	0.790	20.2	24
1.081	0.790	19.5	24
1.081	0.790	18.8	71
1.622	1.186	51.7	307
1.622	1.186	43.8	260
1.622	1.186	39.2	331
1.622	1.186	35.9	260
1.622	1.186	33.4	307
1.622	1.186	31.3	236
1.622	1.186	29.6	260
1.622	1.186	28.0	236
1.622	1.186	26.7	307
1.622	1.186	25.5	283
1.622	1.186	24.4	283
1.622	1.186	23.4	236
1.622	1.186	22.5	307

Li_2SiF_6 g/l	F g/l	Current density A/dm^2	Crack counts cracks/10 mm
1.622	1.186	21.7	402
1.622	1.186	20.9	354
1.622	1.186	20.2	331
1.622	1.186	19.5	449
1.622	1.186	18.8	331
1.622	1.186	18.2	331
1.622	1.186	17.6	331
1.622	1.186	17.1	331
1.622	1.186	16.5	189
1.622	1.186	16.0	142
1.622	1.186	15.5	95
1.622	1.186	15.1	47
1.622	1.186	14.6	24
1.622	1.186	14.2	71
1.622	1.186	13.8	24
1.622	1.186	13.4	47
2.162	1.580	51.7	378
2.162	1.580	43.8	331
2.162	1.580	39.2	354
2.162	1.580	35.4	354
2.162	1.580	33.4	354
2.162	1.580	31.3	402
2.162	1.580	29.6	520
2.162	1.580	28.0	520
2.162	1.580	26.7	520
2.162	1.580	25.5	520
2.162	1.580	24.4	661
2.162	1.580	23.4	615
2.162	1.580	22.5	591
2.162	1.580	21.7	638
2.162	1.580	20.9	709
2.162	1.580	20.2	866
2.162	1.580	19.5	732
2.162	1.580	18.8	843
2.162	1.580	18.2	756
2.162	1.580	17.6	843
2.162	1.580	17.1	866
2.162	1.580	16.5	756
2.162	1.580	16.0	615
2.162	1.580	15.5	378
2.162	1.580	15.1	236
2.162	1.580	14.6	118
2.162	1.580	14.2	71
2.162	1.580	13.8	47
2.162	1.580	13.4	71
2.162	1.580	13.0	0
2.162	1.580	12.6	142
2.162	1.580	12.4	71
2.703	1.976	51.7	354
2.703	1.976	43.8	390
2.703	1.976	39.2	531
2.703	1.976	35.9	496
2.703	1.976	33.4	496
2.703	1.976	31.3	567

Li_2SiF_6 g/1	F g/1	Current density A/dm^2	Crack counts cracks/10 mm
2.703	1.976	29.6	429
2.703	1.976	28.0	602
2.703	1.976	26.7	815
2.703	1.976	25.5	1063
2.703	1.976	24.4	886
2.703	1.976	23.4	921
2.703	1.976	22.5	992
2.703	1.976	21.7	1205
2.703	1.976	20.9	1028
2.703	1.976	20.2	815
2.703	1.976	19.5	850
2.703	1.976	18.8	1098
2.703	1.976	18.2	886
2.703	1.976	17.6	744
2.703	1.976	17.1	461
2.703	1.976	16.5	248
2.703	1.976	16.0	177
2.703	1.976	15.5	47
2.703	1.976	15.1	71
2.703	1.976	14.6	118
3.243	2.372	51.7	602
3.243	2.372	43.8	531
3.243	2.372	39.2	709
3.243	2.372	35.9	709
3.243	2.372	33.4	780
3.243	2.372	31.3	921
3.243	2.372	29.6	886
3.243	2.372	28.0	921
3.243	2.372	26.7	1028
3.243	2.372	25.5	921
3.243	2.372	24.4	780
3.243	2.372	23.4	886
3.243	2.372	22.5	886
3.243	2.372	21.7	850
3.243	2.372	20.9	780
3.243	2.372	20.2	425
3.243	2.372	19.5	213
3.243	2.372	18.8	283
3.243	2.372	18.2	283
3.243	2.372	17.6	157
3.243	2.372	17.1	126
4.324	3.160	51.7	354
4.324	3.160	43.8	591
4.324	3.160	39.2	567
4.324	3.160	35.9	567
4.324	3.160	33.4	602
4.324	3.160	31.3	567
4.324	3.160	29.6	673
4.324	3.160	28.0	744
4.324	3.160	26.7	780
4.324	3.160	25.5	602
4.324	3.160	24.4	744
4.324	3.160	23.4	638
4.324	3.160	22.5	461

Li_2SiF_6 g/l	F g/l	Current density A/dm^2	Crack counts cracks/10 mm
4.324	3.160	21.7	567
4.324	3.160	20.9	638
4.324	3.160	20.2	567
4.324	3.160	19.5	886
4.324	3.160	18.8	886

<u>Sodium fluorosilicate additions</u>

Na_2SiF_6 g/l	F g/l	Current density A/dm^2	Crack counts counts/10 mm
1.304	0.790	51.7	118
1.304	0.790	43.8	118
1.304	0.790	39.2	94
1.304	0.790	35.9	47
1.304	0.790	33.4	47
1.304	0.790	31.3	24
1.304	0.790	29.6	47
1.304	0.790	28.0	24
1.304	0.790	26.7	24
1.304	0.790	25.5	24
1.304	0.790	24.3	24
1.304	0.790	23.4	24
1.304	0.790	22.5	24
1.304	0.790	21.7	47
1.304	0.790	20.9	47
1.304	0.790	20.2	24
1.304	0.790	19.5	24
1.304	0.790	18.8	24
1.304	0.790	18.2	24
1.304	0.790	17.6	24
1.304	0.790	17.1	47
1.304	0.790	16.5	24
1.304	0.790	16.0	47
1.304	0.790	15.5	24
1.304	0.790	15.1	47
1.304	0.790	14.6	24
1.304	0.790	14.2	24
1.304	0.790	13.8	24
1.304	0.790	13.4	24
2.608	1.580	51.7	71
2.608	1.580	43.8	71
2.608	1.580	39.2	47
2.608	1.580	35.9	94
2.608	1.580	33.4	71
2.608	1.580	31.3	94
2.608	1.580	29.6	142
2.608	1.580	28.0	94
2.608	1.580	26.7	118
2.608	1.580	25.5	118
2.608	1.580	24.4	165
2.608	1.580	23.4	118

Na_2SiF_6 g/l	F g/l	Current density A/dm^2	Crack counts cracks/10 mm
2.608	1.580	22.5	95
2.608	1.580	21.7	95
2.608	1.580	20.9	24
2.608	1.580	20.2	47
2.608	1.580	19.5	47
2.608	1.580	18.8	47
2.608	1.580	18.2	240
5.216	3.160	51.7	378
5.216	3.160	43.8	283
5.216	3.160	39.2	354
5.216	3.160	35.9	378
5.216	3.160	33.4	520
5.216	3.160	31.3	992
5.216	3.160	29.6	992
5.216	3.160	28.0	992
5.216	3.160	26.7	1205
5.216	3.160	25.5	1063
5.216	3.160	24.4	1134
5.216	3.160	23.4	1311
5.216	3.160	22.5	1134
5.216	3.160	21.7	1098
5.216	3.160	20.9	1134
5.216	3.160	20.2	1063
5.216	3.160	19.5	992
5.216	3.160	18.8	638
5.216	3.160	18.2	567
5.216	2.160	17.6	307
5.216	3.160	17.1	260
5.216	3.160	16.5	213
5.216	3.160	16.0	189

Potassium fluorosilicate additions

K_2SiF_6 g/l	F g/l	Current density A/dm^2	Crack counts cracks/10 mm
1.529	0.790	51.7	47
1.529	0.790	39.2	47
1.529	0.790	33.4	24
1.529	0.790	29.6	24
1.529	0.790	26.7	24
1.529	0.790	24.4	47
1.529	0.790	22.5	24
1.529	0.790	20.9	24
1.529	0.790	19.5	47
1.529	0.790	18.2	24
1.529	0.790	17.1	24
1.529	0.790	16.0	24
1.529	0.790	15.1	24
3.058	1.580	51.7	283
3.058	1.580	43.8	331
3.058	1.580	39.2	378

K_2SiF_6 g/l	F g/l	Current density A/dm^2	Crack counts cracks/10 mm
3.058	1.580	35.9	354
3.058	1.580	33.4	425
3.058	1.580	31.3	354
3.058	1.580	29.6	544
3.058	1.580	28.0	449
3.058	1.580	26.7	544
3.058	1.580	25.5	472
3.058	1.580	24.4	591
3.058	1.580	23.4	520
3.058	1.580	22.5	661
3.058	1.580	21.7	520
3.058	1.580	20.9	567
3.058	1.580	20.2	425
3.058	1.580	19.5	331
3.058	1.580	18.8	378
3.058	1.580	18.2	213
3.058	1.580	17.6	189
3.058	1.580	17.1	118
3.058	1.580	16.5	118
3.058	1.580	16.0	165
3.058	1.580	15.5	94
3.058	1.580	15.1	71
3.058	1.580	14.6	47
3.058	1.580	14.2	71
6.116	3.160	51.7	354
6.116	3.160	43.8	425
6.116	3.160	39.2	425
6.116	3.160	35.9	520
6.116	3.160	33.4	815
6.116	3.160	31.3	886
6.116	3.160	29.6	886
6.116	3.160	28.0	780
6.116	3.160	26.7	1063
6.116	3.160	25.5	850
6.116	3.160	24.4	780
6.116	3.160	23.4	1063
6.116	3.160	22.5	850
6.116	3.160	21.7	921
6.116	3.160	20.9	673
6.116	3.160	20.2	567
6.116	3.160	19.5	673
6.116	3.160	18.8	544
6.116	3.160	18.2	591
6.116	3.160	17.6	591
6.116	3.160	17.1	591
9.174	4.740	51.7	567
9.174	4.740	43.8	429
9.174	4.740	39.2	567
9.174	4.740	35.9	567
9.174	4.740	33.4	567
9.174	4.740	31.3	709
9.174	4.740	29.6	709
9.174	4.740	28.0	709
9.174	4.740	26.7	709

K_2SiF_6 g/l	F g/l	Current density A/dm^2	Crack counts cracks/10 mm
12.232	6.320	51.7	709
12.232	6.320	43.8	886
12.232	6.320	39.2	709
12.232	6.320	35.9	886
12.232	6.320	33.4	709
12.232	6.320	31.3	744
12.232	6.320	29.6	638
12.232	6.320	28.0	709
12.232	6.320	26.7	496
12.232	6.320	25.5	461
12.232	6.320	24.4	496
12.232	6.320	23.4	496
12.232	6.320	22.5	496
12.232	6.320	21.7	496

Caesium fluorosilicate additions

Cs_2SiF_6 g/l	F g/l	Current density A/dm^2	Crack counts cracks/10 mm
2.831	0.790	51.7	47
2.831	0.790	43.8	47
2.831	0.790	39.2	47
2.831	0.790	35.9	24
2.831	0.790	33.4	24
2.831	0.790	31.3	24
2.831	0.790	29.6	24
2.831	0.790	28.0	24
2.831	0.790	26.7	47
2.831	0.790	25.5	24
2.831	0.790	24.4	24
2.831	0.790	23.4	24
2.831	0.790	22.5	47
2.831	0.790	21.7	47
2.831	0.790	20.9	24
2.831	0.790	20.2	24
2.831	0.790	19.5	24
5.662	1.580	51.7	591
5.662	1.580	43.8	638
5.662	1.580	39.2	496
5.662	1.580	35.9	543
5.662	1.580	33.4	673
5.662	1.580	31.3	709
5.662	1.580	29.6	1028
5.662	1.580	28.0	921
5.662	1.580	26.7	744
5.662	1.580	25.5	1028
5.662	1.580	24.4	1063
5.662	1.580	23.4	921
5.662	1.580	22.5	957
5.662	1.580	21.7	567
5.662	1.580	20.9	496
5.662	1.580	20.2	319
5.662	1.580	19.5	236
5.662	1.580	18.8	47

Cs_2SiF_6 g/l	F g/l	Current density A/dm^2	Crack counts cracks/10 mm
5.662	1.580	18.2	142
5.662	1.580	17.6	94
5.662	1.580	17.1	47
7.520	2.102	51.7	602
7.520	2.102	43.8	886
7.520	2.102	39.2	1028
7.520	2.102	35.9	850
7.520	2.102	33.4	957
7.520	2.102	31.3	1063
7.520	2.102	29.6	1063
7.520	2.102	28.0	815
7.520	2.102	26.7	709
7.520	2.102	25.5	709
7.520	2.102	24.4	496
7.520	2.102	23.4	354
7.520	2.102	22.5	177
7.520	2.102	21.7	189
7.520	2.102	20.9	236
7.520	2.102	20.2	354
11.324	3.160	No cracking	

<u>Ammonium fluorosilicate additions</u>

$(NH_4)_2SiF_6$ g/l	F g/l	Current density A/dm^2	Crack counts cracks/10 mm
1.236	0.790	51.7	260
1.236	0.790	43.8	165
1.236	0.790	39.2	118
1.236	0.790	35.9	118
1.236	0.790	33.4	94
1.236	0.790	31.3	94
1.236	0.790	29.6	94
1.236	0.790	28.0	189
1.236	0.790	26.7	94
1.236	0.790	25.5	118
1.236	0.790	24.4	118
1.236	0.790	23.4	94
1.236	0.790	22.5	118
1.236	0.790	21.7	213
1.236	0.790	20.9	47
1.236	0.790	20.2	118
1.236	0.790	19.5	94
1.236	0.790	18.8	47
1.236	0.790	18.2	24
1.236	0.790	17.6	118
1.236	0.790	17.1	94
1.236	0.790	16.5	24
1.236	0.790	16.0	71
1.236	0.790	15.5	94
1.236	0.790	15.1	47
2.472	1.580	51.7	331
2.472	1.580	43.8	496

$(NH_4)_2SiF_6$ g/l	F g/l	Current density A/dm^2	Crack counts cracks/10 mm
2.472	1.580	39.2	544
2.472	1.580	35.9	429
2.472	1.580	33.4	449
2.472	1.580	31.3	567
2.472	1.580	29.6	472
2.472	1.580	28.0	496
2.472	1.580	26.7	496
2.472	1.580	25.5	520
2.472	1.580	24.4	685
2.472	1.580	23.4	615
2.472	1.580	22.5	591
2.472	1.580	21.7	615
2.472	1.580	20.9	591
2.472	1.580	20.2	567
2.472	1.580	19.5	661
2.472	1.580	18.8	638
2.472	1.580	18.2	615
2.472	1.580	17.6	590
2.472	1.580	17.1	401
2.472	1.580	16.5	354
2.472	1.580	16.0	283
2.472	1.580	15.5	165
2.472	1.580	15.1	71
2.472	1.580	14.6	94
2.472	1.580	14.2	71
2.472	1.580	13.8	47
2.472	1.580	13.4	24
2.472	1.580	13.0	118
3.708	2.372	51.7	815
3.708	2.372	43.8	886
3.708	2.372	39.2	815
3.708	2.372	35.9	1063
3.708	2.372	33.4	780
3.708	2.372	31.3	1028
3.708	2.372	29.6	992
3.708	2.372	28.0	957
3.708	2.372	26.7	850
3.708	2.372	25.5	921
3.708	2.372	24.4	850
3.708	2.372	23.4	850
3.708	2.372	22.5	673
3.708	2.372	21.7	602
3.708	2.372	20.9	213
3.708	2.372	20.2	284
3.708	2.372	19.5	236
3.708	2.374	18.8	284
3.708	2.374	18.2	284
4.944	3.160	51.7	638
4.944	3.160	43.8	544
4.944	3.160	39.2	780
4.944	3.160	35.9	756
4.944	3.160	33.4	756
4.944	3.160	31.3	879
4.944	3.160	29.6	850

$(NH_4)_2SiF_6$ g/l	F g/l	Current density A/dm^2	Crack counts cracks/10 mm
4.944	3.160	28.0	709
4.944	3.160	26.7	815
4.944	3.160	25.5	673
4.944	3.160	24.4	733
4.944	3.160	23.4	602
4.944	3.160	22.5	496
4.944	3.160	21.7	673
4.944	3.160	20.9	709
4.944	3.160	20.2	815
4.944	3.160	19.5	815
7.416	4.740	51.7	236
7.416	4.740	43.8	449
7.416	4.740	39.2	496
7.416	4.740	35.9	402
7.416	4.740	33.4	472
7.416	4.740	31.3	472

Hydrofluosilicic acid additions

H_2SiF_6 g/l	F g/l	Current density A/dm^2	Crack counts cracks/10 mm
0.500	0.395	51.7	71
0.500	0.395	43.8	47
0.500	0.395	39.2	47
0.500	0.395	35.9	47
0.500	0.395	33.4	47
0.500	0.395	31.3	47
0.500	0.395	29.6	47
0.500	0.395	28.0	24
0.500	0.395	26.7	24
0.500	0.395	25.5	24
0.500	0.395	24.4	24
0.500	0.395	23.4	47
0.500	0.395	22.5	24
0.500	0.395	21.7	24
0.500	0.395	20.9	24
0.500	0.395	20.2	24
1.000	0.790	51.7	24
1.000	0.790	43.8	71
1.000	0.790	39.2	47
1.000	0.790	35.9	24
1.000	0.790	33.4	24
1.000	0.790	31.3	71
1.000	0.790	29.6	24
1.000	0.790	28.0	71
1.000	0.790	26.7	47
1.000	0.790	25.5	47
1.000	0.790	24.4	24
1.000	0.790	23.4	71
1.000	0.790	22.5	24
1.000	0.790	21.7	71

H_2SiF_6 g/1	F g/1	Current density A/dm^2	Crack counts cracks/10 mm
1.000	0.790	20.9	47
1.000	0.790	20.2	47
1.000	0.790	19.5	47
1.000	0.790	18.8	24
1.000	0.790	18.2	47
1.000	0.790	17.6	24
1.000	0.790	17.1	24
2.000	1.580	51.7	429
2.000	1.580	43.8	354
2.000	1.580	39.2	429
2.000	1.580	35.9	378
2.000	1.580	33.4	429
2.000	1.580	31.3	429
2.000	1.580	29.6	472
2.000	1.580	28.0	429
2.000	1.580	26.7	520
2.000	1.580	25.5	591
2.000	1.580	24.4	591
2.000	1.580	23.4	615
2.000	1.580	22.5	567
2.000	1.580	21.7	662
2.000	1.580	20.9	662
2.000	1.580	20.2	472
2.000	1.580	19.5	354
2.000	1.580	18.8	283
2.000	1.580	18.2	236
2.000	1.580	17.6	142
2.000	1.580	17.1	94
2.000	1.580	16.5	47
2.000	1.580	16.0	71
2.000	1.580	15.5	47
2.000	1.580	15.1	47
3.000	2.372	51.7	591
3.000	2.372	43.8	591
3.000	2.372	39.2	591
3.000	2.372	35.9	685
3.000	2.372	33.4	780
3.000	2.372	31.3	567
3.000	2.372	29.6	709
3.000	2.372	28.0	733
3.000	2.372	26.7	780
3.000	2.372	25.5	756
3.000	2.372	24.4	709
3.000	2.372	23.4	685
3.000	2.372	22.5	615
3.000	2.372	21.7	661
3.000	2.372	20.9	260
3.000	2.372	20.2	307
3.000	2.372	19.5	260
3.000	2.372	18.8	236
3.000	2.372	18.2	283
3.000	2.372	17.6	236
4.000	3.160	51.7	591
4.000	3.160	43.8	567

H_2SiF_6 g/l	F g/l	Current density A/dm^2	Crack counts cracks/10 mm
4.000	3.160	39.2	591
4.000	3.160	35.9	591
4.000	3.160	33.4	709
4.000	3.160	31.3	472
4.000	3.160	29.6	472

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